AN EXPERIMENTAL STUDY ON IRON AND MANGANESE REMOVAL AND OPTIMUM OPERATING CONDITIONS FOR A SMALL WATER TREATMENT SYSTEM

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by

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ABSTRACT

In sparse rural communities, it is often not cost-efficient to construct large or medium-scale water treatment plants or to connect to existing municipal facilities. In Newfoundland, many rural communities are facing similar situations in terms of drinking water supply, and a potable water dispensing unit (PWDU) was previously developed in order to supply reliable and safe drinking water to these communities. While the initial testing of this treatment system demonstrated its reliability in meeting drinking water standards, the insufficient removal of colour present in treated water occurred in some cases, which is often caused by high levels of iron and/or manganese. Aimed to improve the performance of the PWDU in removing iron and manganese, this study used a combination of central composite design and response surface model approaches to evaluate iron and manganese removal efficiencies under varying operational (e.g. ozone doze and flow rate) and environmental conditions (i.e., concentration of iron and manganese). In terms of iron removal efficiency, the initial iron concentration in the influent had the strongest effect followed by influent manganese concentration, while flow rate and ozone dose had no significant effect on iron removal efficiency. In terms of manganese removal efficiency, all 4 factors analyzed had significant effects but the flow rate had the weakest effect when compared to the effects of initial iron (strongest) and manganese (second strongest) concentrations. The results also indicated that an ozone dose of 8.5 g/hr was optimal for iron and manganese removal in most cases tested. While higher flow rate was preferred for raw water with lower iron and manganese concentrations, lower flow rate was better for raw water with higher iron and manganese concentrations. This study greatly improved our knowledge in system performance as well as iron and manganese removal by the PWDU, which would benefit the water treatment industry as well as the rural communities across NL by improving the quality and capacity of drinking water supply. In addition, the experimental approaches used by this study also provided a useful reference and tool for further studies aimed to improve the performance of small-scale water treatment systems.

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TABLE OF CONTENTS

CHAPTER 3 MATERIALS AND METHODS

CHAPTER 4 RESULTS AND DISCUSSION

CHAPTER 5 CONCLUSIONS AND RECOMMENDATIONS

LIST OF TABLE

LIST OF FIGURE

LIST OF ABBREVIATIONS

ANOVA	Analysis of Variance
CCD	Central Composite Design
DE	Diatomaceous Earth
DOE	Design of Experiments
GAC	Granular Activated Carbon
ICP-MS	Inductively coupled plasma mass spectrometry
LFB	Laboratory Fortified Blank
LRB	Laboratory Reagent Blank
MCL	Maximum contaminant level
MDL	Method Detection Limit
NF	Nanofiltration
PAC	Powdered activated carbon
PWDUs	Potable Water Dispensing Units
QCS	Quality Control Sample
RSM	Response surface methodology
RO	Reverse Osmosis
SDWA	Safe Drinking Water Act
SWTPs	Small Water Treatment Plants
SCADA	Supervisory Control and Data Acquisition
TK	Tank

THMs	Trihalomethanes
UV	Ultraviolet Light
USEPA	United States Environmental Protection Agency
WHO	World Health Organization

CHAPTER 1 INTRODUCATION

1.1 Background

Providing safe drinking water for remote communities faces many challenges as it is often not technically feasible or cost-efficient to connect the small and sparse communities to large or medium-scale water treatment facilities in cities. At the same time, the limitation in terms of available resources (e.g. manpower, technology) for effective water treatment in rural communities makes such task difficult. Traditionally, people live in rural areas utilize wells as the main source of drinking water. Although wells provide a bare minimum solution for rural communities, the reliability and quality of the drinking water produced from the wells are questionable. In addition, well water is also vulnerable to various potential sources of contamination, such as run-offs or septic contaminations, and the lack of effective treatment could lead to disease outbreaks. For example in 2000, the drinking water supply systems of Walkerton in Ontario was contaminated by *E. coli* carried with run offs from nearby farms, which led to the death of 7 people and left 2,500 sick (PEO, 2001). Although boiling may help to reduce the chance of such outbreak in some cases, it does very little to remove the impurities (organic or inorganic) from the well water that is often marked by unpleasant taste and odour (Arvai and Post, 2012). Therefore, potable water treatment plants are needed for these communities as the presence of some of the contaminants in drinking water that may cause health concerns due to their toxicity and carcinogenicity.

In rural Newfoundland and Labrador, the population is widely dispersed over large areas. According to the population consensus, 53.39% of the 514,058 residents in NL,

(274,456 residents) live in rural areas (defined as location with population density below 150 persons per square kilometer) (Statistics Canada, 2011). Such demography has major effects on the strategy of producing drinking water. The province of Newfoundland and Labrador is blessed with plentiful freshwater resources, but each water source has unique water chemistry that is influenced by the potential for contamination according to its location and the development activities within its watershed area.

Several water treatment strategies are used in the province to address different scenarios, and to provide unique solutions to treat the water consumed. A full-scale water treatment plant is not always a feasible solution for any community. An alternative solution to the treatment challenge for smaller communities is the use of small scale drinking water treatment systems; referred to as potable water dispensing units (PWDUs) hereafter, which are configured for treatments that respond to a community's specific drinking water quality issues. By the end of March 2010, there were 23 water treatment plants serving Newfoundland, and 7 of which are potable water dispensing units. In addition, the Department of Municipal Affairs approved 23 applications for PWDU funding by the end of the 2010 fiscal year, which will be used towards PWDU installation in these small communities. In terms of disinfection, chlorination is by far the most frequently used method in the province, and there are 443 chlorination systems across the province (WRMD, 2010). However, chlorine can create disinfection by-products such as trihalomethanes (THMs) and haloacetic acids (HAAs) that are harmful for human health and the environment. In order to avoid generating such impact, Fay environmental developed a PWDU that disinfects water without the usage of any chemicals.

1.2 Statement of Problems

Although the PWDU developed by Fay is successful in terms of producing reliable drinking water for rural communities, it is a fact that there is still space and a need for improvement as two major technical challenges have been identified through field applications. The first technical challenge is the removal of colour, which is occasionally present in the treated water even though the drinking water standards have been met. Experience has indicated that relatively high levels of iron chelates and complexes (e.g., $\geq$ 200 μg/L) and/or manganese (e.g., $\geq$ 150 μg/L) combined with colour values of 100 mg/L PtCo equivalent or greater would cause particular difficulties in treating the water (FECL, 2009). In agreement with this technical challenge encountered by the PWDU developed by Fay, a recent study evaluating PWDUs in 7 different communities across Newfoundland also found presence of color and manganese above drinking water standard in treated water in some cases (Bishop, 2010). In these instances, it is strongly advised that lab experiment and prolonged pilot trials are to be undertaken to remove the color of the water by addition of other treatment methods. The second technical challenge is how to optimize the operation of the system in order to make it more robust and cost-efficient as well as adaptive to variations in operational and environmental conditions (e.g., quality of raw water) affected by natural and/or anthropogenic events. The optimization of the water treatment operation is often perceived as unnecessary given that the system is already designed to meet our requirements (Rivas et al., 2008; Tang and Ellis, 1994). However, with any design, operating margin exists, thus it is key to manage performance degradation. For example, the optimization of water treatment operation can

reduce its power consumption by 20-30%, maintenance work by 50%, while increase its life-time by 10-20% (Eswaramoorthi, 2009; Jimbo and Goto, 2001). In addition, the optimization of water treatment procedures would also ensure the quality of treated water meets the drinking water standard under different environmental conditions.

1.3 Research Objectives

In order to help solving the above technical challenges, this research aims to examine the effects of operational parameters (i.e., flow rate and ozone dose) and raw water quality (i.e., initial manganese and iron concentrations) on removal efficiencies for iron and manganese. Furthermore, this research also seeks to determine the optimum operational conditions through experimental tests. To achieve this goal, the following tasks were conducted:

- To collect and analyze the operational data and characterize the water treatment system (i.e., PWDU).
- To design experiment and analyze the data collected using Design Expert.
- To monitor the quality of the raw water under different operational and environmental conditions.
- To make recommendations for optimal operational parameters that improves drinking water treatment.
- To identify important factors affecting iron and manganese removal efficiencies of small scale water treatment systems.

1.4 Research significance

This research will help to improve the implementation of the water treatment technology as well as the small-scale drinking water treatment industry in the following ways: 1) the water treatment data collected in this study will help us to assess the functionality of the PWDU in the context of iron and manganese removal; 2) the optimization of operational parameters conducted in this study will help to guide operational practices that are best suited for the system and the working environment; 3) the experimental approach developed in the study can serve as a template that is applicable to any other small scale water treatment systems.

1.5 Layout of Thesis

This thesis is divided into 5 chapters. Following the Introduction, Chapter 2 consists of a review of recent literature relevant to drinking water treatment. PWDU-related technologies, and the configurations of PWDUs with respect to the manganese and iron removal.

Chapter 3 describes the experimental design and procedures used to evaluate the performance of the PWDU in terms of iron and manganese removal at various environmental and operational conditions.

Chapter 4 presents, interprets, and discusses the experiment and the results for the performance evaluation of the PWDU in terms of iron and manganese removal.

Chapter 5 summarizes the main findings and discusses the significance of this research work. Based on these findings, recommendations were made for future research taking the issues encountered in the current study into account.

CHAPTER 2 LITERATURE REIVEW

2.1 Small Water Treatment Plants

Contaminated water sources are potential vehicles for the transmission of waterborne diseases such as cholera, shigellosis and campylobacteriosis (Ashbolt, 2004; Momba et al., 2006). It was estimated that about 1.1 billion people globally have no access to safe water and the vast majority (88%) of diarrhoeal diseases in the world are attributable to contamination in drinking water, sanitation and hygiene. Approximately 3.1% of annual deaths (1.7 million) and 3.7% of the annual health burden (disability adjusted life years) (54.2 million) world-wide are attributable to unsafe water, sanitation and hygiene (WHO, 2003). In order to provide safe drinking water in rural and peri-urban areas, water sources are usually treated by small scale water treatment plants.

Small water treatment plants (SWTP) are defined as water treatment systems installed in areas which are not adequately serviced and do not normally fall within the boundaries of urban areas (Makungo et al., 2011). Frequently, small scale water supplies are defined based on legislatively specified criteria, such as population size, quantity of water provided, number of service connections or the type of supply technology used. Regardless of the criteria or terms are used to separate small scale water supplies from their large scale counterparts, physical size is not the deciding factor that sets them apart. Instead, the administrative, managerial, and operational characteristics, conditions and challenges play more important roles in defining a water treatment plant (Obi et al., 2008).

SWTPs can be established in remote and sparsely populated regions where the access to large scale drinking water supply facilities is limited. Therefore, SWTPs serve as a viable option for drinking water production in rural communities. Recognizing the importance of SWTPs in delivering safe drinking water to small communities, governments and industries as well as research institutions across the world have devoted much effort in the development and implementation of such systems. In the United States, for example, approximately 160,000 SWTPs including 50,000 community-based systems and 110,000 non-community-based (e.g. commercial, military purposes) systems are used to provide drinking water for over 68 million people (Patterson et al., 2005). In Europe, approximately 30% of the total population live in rural areas where small scale water supplies prevail. In Germany, for example, about 20% of the population (or 16 million people) receive water from more than 3,300 SWTPs, while about 700,000 people still use water from some 185,000 private wells (WHO., 2011). At the same time, SWTPs face a number of challenges, one of which being the need to improve the quality and reliability of water treatment. Using the U.S. again as an example, of the 160,000 SWTPs in service, nearly 77% of the systems in service are observed for violation of the Maximum Contaminant Level (MCL), which contribute to 94% of incompliance with the Safe Drinking Water Act (SDWA) violations. Furthermore, ever-increasing numbers of regulations and regulated contaminants require constant improvement of SWTPs and optimization of their operation (Patterson et al., 2005).

Canada has approximately a quarter of world's freshwater supply in its streams and lakes, providing ample sources of drinking water for its inhabitants. Unfortunately, much of the freshwater resource is unavailable to the 90% of the population who live within

300 kilometers of the country's southern border (Peterson and Torchia, 2008) and the population in small communities across the nation face many challenges in utilizing their local freshwater supplies for drinking water. The mismatch between water resource and population distribution has led to stress on some water supplies in densely populated regions while inadequate treatment in sparsely populated areas. In recent years, water quality issues have come to the forefront of public concerns across the country. For example, in 2000, the municipal groundwater supply of Walkerton, Ontario, became contaminated with the deadly bacteria *Escherichia coli* O157:H7, which resulted hundreds becoming sick and ultimately the deaths of seven people (PEO, 2001). In 2001, an outbreak of the parasite cryptosporidium was reported in the community of North Battleford in Saskatchewan, which lead to the death of 4 people, and left at least 44 others sick (PEO, 2001). This potentially lethal single-cell parasitic cryptosporidium has also surfaced in water supplies in British Columbia communities of Cranbrook and Kelowna. Faecal coliforms, including *E. coli*, have been detected in drinking water in Moncton, New Brunswick. In addition, cancer-causing trihalomethanes (THMs) have been reported in drinking water sources in Newfoundland (Christensen, 2001). In June 2000, approximately 130 boil orders were in place in Newfoundland affecting about 10% of the province's population (Health and Community Services, 2000). These outbreaks demonstrated the importance in proper treatment of drinking water to eliminate contaminants that are damaging to the health of consumers.

2.2 Regulatory Review

In Canada, provincial governments play major roles in drinking water management and governance while the role of federal government is limited. In 1867, the Constitution Act gave provinces the jurisdiction to govern their own water resources, and the provinces were also responsible for day-to-day water resource management. On the other hand, the jurisdiction of the federal government in water resource is limited to very specific aspects, such as fisheries, navigation, and external affairs. This province-based regime in water resource management would introduce discrepancies in water resource management across the nation.

Recognizing the need to unify and improve water resource management, the federal government passed the Canada Water Act in 1970 and created the Department of the Environment in 1971, entrusting the Inland Waters Directorate with providing national leadership for freshwater management. Boil-water advisories are intended to be emergency measures to protect consumers from imminent but temporary threats to drinking water safety. Long-term continuing or recurring advisories, regardless of their underlying rationale, are a frank admission that the affected systems are otherwise failing to assure safe drinking water. National leadership in Canadian freshwater management is not only a national interest, but also brings several benefits to the provinces and industrial sectors. Since it foundation, Environment Canada has been actively promoting a partnership approach that combines the interests of various levels of government and private sector to seek for the optimal management and sustainable use of the water resource. For example, Canada-wide hearings were conducted in 1984/85 to consult the public in order to develop a federal water policy that is compatible with the interests of various parties. Guided by the findings of the inquiry, the government released its Federal

Water Policy in 1987, which has since given focus to the water-related activities of all federal departments and which will continue to provide a framework for action in the coming years as it evolves in light of new issues and concerns.

The technical expertise in many Canadian water providers is certainly on par with the best in the world, a management structure that is ill-suited to the task, complacency, some misunderstanding of key safety issues and an overall lack of leadership would still jeopardize the drinking water quality (Hrudey, 2011). For example, a serious drinking water outbreak in North Battleford, Saskatchewan in 2001 still remand federal and provincial health officials to remain vigilant for any signs of deficiencies in drinking water quality. Although deficiencies in public drinking water quality no longer pose health risk to consumers in most of urbanized Canada, Canadians in remote, smaller communities do not have the same assurance for drinking water quality (Hrudey et al., 2008). One of the major obstacles in improving drinking water quality in small communities is the complacency with the minimum drinking water standard. In many cases, it is impossible for the regulators to bring these smaller communities up to the best-practice standard simply because these communities are reluctant to allocate more financial and training support to improve drinking water quality. Many of these communities are complacent about promoting the level of competence required for assuring safe drinking water, as they continue to provide the bare minimum financial compensation and training support. The extent of this problem has been evident in the large number (over 1,700 reported in a national survey in 2008) of ongoing boil-water advisories in Canada, many of which have been in place for months or even years (Eggertson, 2008).

2.3 Technologies Used in Small Scale Water Treatment

Most small scale water treatment systems treat drinking water so that it will be safe and reliable for the consumer. The application of specific treatment technologies depend on source water quality, system size, and operating sophistication. The individual treatment technologies are designed to be effective in removing one or more types of contaminants including particulate, chemical and biological contaminants. Depending upon the type of contamination present in the source water, one or more treatment technologies may be applied to the small scale water treatment systems to provide safe drinking water to consumers. A review of commonly used treatment technologies to remove particulate, and contaminants is presented in this section.

2.3.1 Filtration

Filtration is a process for removing particulate matter from water by passage through porous media, and it is a universally used technology in drinking water treatment. The term 'primary filtration' is in reference to the fact that it serves to remove larger particulate matters by a simple filtration through media (e.g., sand filter) or bag and/or cartridge filters. On the other hand, advanced filtration techniques usually involve more sophisticated technologies such as the membrane filtration. Some of these filtration technologies (slow sand filtration, diatomaceous earth etc.) are capable of removing more than 99% of the bacteria and viruses from water if properly operated (Jefferson et al., 2000). In addition, some of these technologies are also effective in removing larger microorganisms such as cysts, ova and schistosomes (Zhou and Smith, 2001).

In a typical simple filtration technology, loose granular materials such as sand are often used as filter media, which is easily produced in large scale. The type of filter media most suited for an application depends mainly on the impurities present in the source/raw water. Specifically, the size range of the impurities present in the raw water typically dictates the type of filter media. The particle sizes of common water contaminants and the corresponding filtration devices required for their treatment (or removal) are shown in Figure 2.1. There are numerous types of filtration processes, and some of the common filtration processes are discussed in the sections follow.

2.3.1.1 Simple Filtration

Slow sand filtration is a process where untreated water percolates slowly down through a layer of fine sand, then through a layer of gravel, and ultimately collects in a system of under drains. Slow sand filter is essentially a tank containing a bed of fine sand that is 0.9-1.2 m thick. This filter works by a combination of biological action, absorption and straining. Its most important feature is the sticky deposit called the "schmutzdecke" lay which forms on the very top of the sand. This biological layer traps small particles, and also helps to degrade the organic matter present in water. In this layer, bacteria and microscopic plants multiply to form a very fine straining mat in the topmost few millimeters. Micro-organisms dwell in the mat and deeper in the sand feed on any trapped pathogens as water flows through the matrix, greatly improving water quality. Diatomaceous earth (DE) is another simple filtration technology that is frequently used in water treatment plants. DE is a natural material that can be used directly to treat low turbidity raw water supplies or chemically coagulated, more turbid water sources. DE

filters consist of a pre-coat layer of DE, approximately 1/8-inch thick, supported by a septum or filter element (USEPA, 1998).

Having several advantages over single-media filters, multi-media filters often consist of several layers of filtering media that differ in pore size and density. For example, a multi-media filter could be made of layers of media with low density (e.g. coarse coal) overlaying media with higher density (e.g. sand, garnet, and gravel) (Figure 2.1). The purpose of using media with distinct densities is to ensure the stratification of these filtration media in a way that anthracite overlays sand that overlays the garnet, The main advantages of multimedia filters over single-medium filters include longer filtration duration, higher filtration rates, and a greater capacity to filter water with higher turbidity and suspended solids. These characteristics of multi-media filters owe to the higher storage capacity of these filters as opposed to the low storage capacity in single-medium filters. This is because in single-medium filters, the pore volume can be utilized for storage is restricted within the top portion of the medium, as initial storage of solids in the surface will make pores below inaccessible. On the other hand, in a multimedia filter, the access to pores is no longer blocked by the initial accumulation of solids, resulting deep penetration of solids into the media. Given these disadvantages comparing to multi-media filters, single-medium filters are rarely used in wastewater or advanced wastewater treatment, while multimedia filters are frequently used in advanced or tertiary wastewater treatment given their large capacities in floc storage (te Poele et al., 2005).

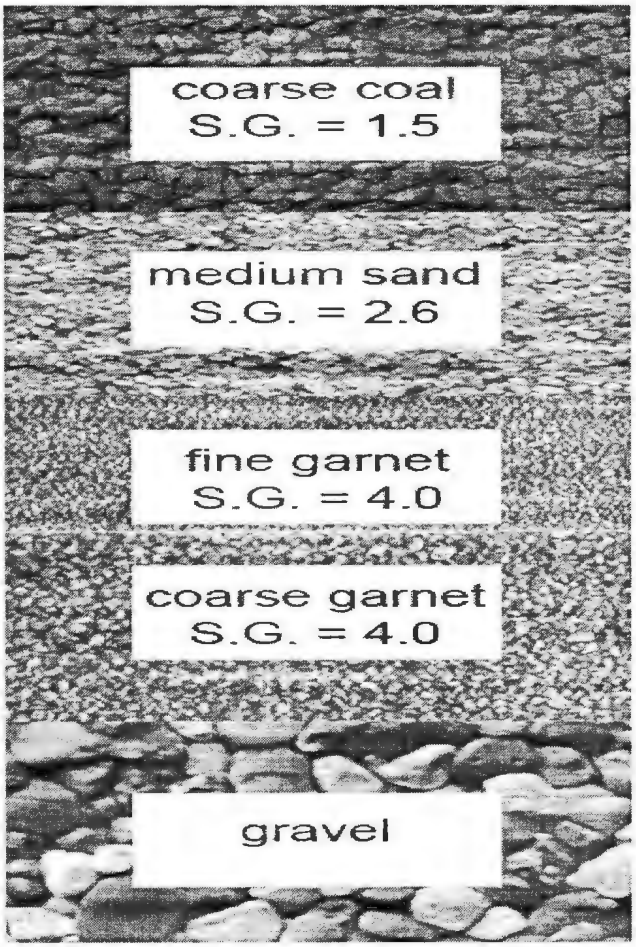


Figure 2.1 Multimedia filter configuration, specific gravity (S.G) (Minerals, 2009)

2.3.1.2 Advanced filtration

Membrane filtration is a pressure driven separation process in which particulate matter larger than one micrometer is rejected by an engineered barrier, primarily through a size-exclusion mechanism. The removal efficiency for a target organism can be measured and verified through the application of a direct integrity test (EPA, 2003a). Some common types of membrane filtration are microfiltration, ultrafiltration, and nanofiltration. Microfiltration is a pressure-driven membrane filtration process that typically employs hollow-fiber membranes with a pore size range of approximately 0.1 – 0.2 micrometers (nominally 0.1 micrometers). Ultrafiltration is a pressure-driven

membrane filtration process that typically employs hollow- fiber membranes with a pore size range of approximately 0.01 – 0.05 micrometer (nominally 0.01 micrometers). Nanofiltration is a pressure-driven membrane separation process that employs the principles of reverse osmosis to remove dissolved contaminants from water and is typically applied for membrane softening or the removal of dissolved organic contaminants (USEPA, 2003).

Figure 2.2 Particle size distribution of common contaminants and associated filtration technology (USEPA, 2003)

2.3.2 Sorption

Ion exchange and sorption technologies are commonly used in chemical contaminants removal. The rest of this section is a brief overview of these technologies along with some other treatment techniques that are used to remove chemical contaminants in drinking water. Adsorption is involved in the removal of ions and molecules from solution by their enrichment on the surface of adsorbents. Adsorption is driven by the interfacial forces of the ions and the adsorbent. Adsorption media employed at drinking water plants include granular activated carbon, activated alumina, and iron media. Sorption technologies are used for the removal of organics, taste and odor, and inorganic contaminants.

2.3.2.1 Activated Carbon

Activated carbon is produced by exposing carbon to very high temperatures that create a vast network of internal pores. Two types of activated carbon, granular and powdered, are used widely in drinking water treatment. Powdered activated carbon (PAC), which is frequently used for taste and odor control, is added directly to raw water and subsequently removed by settling in sedimentation basins. PAC and GAC serve to remove many organic contaminants as well as taste and odor from water supplies. GAC removes contaminants through adsorption, primarily a physical process in which dissolved contaminants adhere to the porous surface of the carbon particles. In some cases, the adsorption process can be reversed relatively easily. The ease of reversing adsorption is another key factor in activated carbon's usefulness because it facilitates the recycling or reuse of the carbon (NDWC, 1997).

2.3.2.2 Ion Exchange

Ion exchange involves the selective removal of charged inorganic species from water using an ion-specific resin. The surface of the ion exchange resin contains charged functional groups that retain ionic species by electrostatic attraction. As water containing undesired ions passes through a column of resin beds, charged ions on the resin surface are exchanged for the undesired species (e.g. Mg^{2+} and Ca^{2+}) in the water. The resin, when saturated with the undesired species, is regenerated with a solution of the exchangeable ion (USEPA, 1998).

2.3.3 Disinfection

Disinfection is a process for reducing the number of pathogenic microbes in water and is required by the Surface Water Treatment Rule (SWTR) for all PWSs that obtain their water from surface water or ground water under the influence of surface water. In addition, PWDUs must maintain a residual level of disinfectant in the distribution system. It is required that, at the point where the water enters the distribution system, the residual disinfection concentration should not fall below 0.2 mg/L. In addition, the residual disinfection concentration must be maintained throughout the distribution system such that non-detection results are measured in no more than 5% of the samples collected each month.

2.3.3.1 Chlorination

Chlorine is the most common method used for disinfection. Although people are increasingly concerned about disinfection by-products of chlorine, it remains the most popular disinfection method used in drinking water treatment given its effectiveness

against common pathogens and organic impurities. The effectiveness of chlorine can be easily tested by measuring the residual chlorine at the point of consumption to ensure proper disinfection. The oxidative potential of chlorine also makes it an effective agent against organic impurities present in water. However, the disinfection by-products produced by chlorination are known to have carcinogenic properties. Other disadvantages of chlorination also include undesirable tastes and odors, requirement of additional equipment (such as tanks) to guarantee proper contact time, and extra time to monitor and ensure proper residual concentration level. In addition, it also performs poorly in removing viruses (such as enterovirus and hepatitis A) and protozoa (such as Cryptosporidia and Giaradia) (USEPA, 2003).

There are a number of methods of delivery and chemical reactions utilized for chlorination. These include chlorine gas, chloramines, chlorine dioxide, and sodium hypochlorite. The common goal of all these methods is to release free chlorine in the form of hypochlorite, or in the case of chloramines, combined available chlorine (NH_2Cl and $NHCl_2$) (Schmittinger et al., 2000).

2.3.3.2 Ultraviolet Irradiation (UV)

The use of UV light as means of water disinfection has been a proven process for many years. As contaminated water is exposed to UV light, the genetic materials of organisms exposed to UV are disrupted, which leads to their inactivation. A special lamp generates the radiation that creates UV light by striking an electric arc through low-pressure mercury vapor (low-pressure UV). This lamp emits a broad spectrum of radiation with intense peaks at UV wavelengths of 253.7 nanometers (nm) and a lesser

peak at 184.9 nm. Research has shown that the optimum UV wavelength range for the destruction of bacteria is between 250 nm to 270 nm. At shorter wavelengths (e.g.185 nm), UV light is powerful enough to produce ozone, hydroxyl, and other free radicals that also help to destroy bacteria (USEPA, 2003).

One benefit of the UV disinfection process is the elimination of chemical usage in drinking water treatment. Unfortunately, it is not suitable for water with high levels of suspended solids, turbidity, color, or soluble organic matter, as UV can be blocked or absorbed by such impurities, reducing disinfection performance. Unlike chlorination, the lack of disinfection residual by UV disinfection also limits its effectiveness in disinfection. In addition, UV disinfection also faces many challenges including the lack of technical database on the performance of UV systems with various water sources, standardized mechanism to measure, calibrate, or certify the performance of the equipment before or after installation (Richardson, 2003).

2.3.3.3 Ozonation

Ozonation is another common disinfection method for drinking water treatment. Ozone is a strong oxidant that reacts with many organic and inorganic compounds present in water. Ozone is used to eliminate tastes and odors by breaking down organic compounds and odors by breaking down organic compounds, and it also facilitates the removal of iron and manganese by oxidizing these compounds to less soluble forms. The oxidization of iron and manganese need to be completed before residual ozone is available for disinfection. Therefore, the amount of iron and manganese present in water

play very important roles in dictating the amount of ozone required for sufficient disinfection.

As ozone is very unstable, it should be generated as needed at the point of application. The generation of ozone is achieved by combining an oxygen atom with an oxygen molecule (O_2), ($3O_2 \Leftrightarrow 2O_3$). This reaction is endothermic thus requires a considerable input of energy.

Ozone is a colorless, very unstable gas that is effective as an oxidizing agent in removing bacteria within a relatively short exposure time. Since ozone is unstable and has a very short life, ozone generators are used to produce ozone gas on site as needed. These generators must be installed and monitored cautiously, as high concentration levels of ozone will oxidize and deteriorate all downstream piping and components. With home ozone systems, leftover ozone must be removed with an off-gas tank to ensure homeowners are not exposed to ozone gas, which is a strong irritant. In addition, ozone reacts with bromide resulting in the formation of highly carcinogenic DBPs including bromate, bromoform, and dibromeacetic acid. In PWDUs, UV equipment or biological filters are typically installed to remove ozone residuals prior to filtration (EPA, 2003). Comparing with other disinfection method, the most prominent advantage of ozone is the fact it leaves residuals that prolong the duration of the disinfection process.

2.3.4 Summary

A small water treatment system often integrates a multiple of technologies to remove various types of contaminants. Depth filtration processes with a range of pore sizes are used to remove particles of various sizes. Anthracite and sand are frequently

used to remove particulate matter, and activated carbon is also frequently used to absorb impurities. To ensure the sanitation of treated water, sterilization procedures using UV and chlorination are also included as treatment procedures. In order to remove some ions (e.g. iron and manganese) and organic materials, ozonation is also incorporated into many systems.

Since the overall performance of a small scale water treatment system depends on the effectiveness of each and every procedure, numerous studies have been conducted to evaluate and optimize these different treatment procedures. A study conducted in Cincinnati optimized the oxidization process used in a small scale water treatment plant to remove Methyl tert-Butyl Ether (Sinha et al., 2007). In Algarve, Portugal, the ultra-filtration performance was evaluated using water subjected to various physical and chemical pre-treatment in Alcantarilha's water treatment systems. Methyl Tert-Butyl Ether (MTBE) is a gasoline additive that poses a major threat to the drinking water quality in small communities in Puerto Rico. In order to remove this organic contaminant, a combinational use of UV and ozone were optimized for application in small scale water treatment systems, which ultimately lead to the development of an advanced oxidation processes package for these systems. Since most rural communities have limited human and technological resources, the water treatment plants for rural communities need to be compact, reliable, and easy to maintain and operate. These requirements presented many challenges for drinking water treatment in rural communities.

2.4 Common Schema for Small Water Treatment Plants

The primary purpose of drinking water treatment is to render the water fit for human consumption. This requires the elimination of impurities and pathogens. Secondary purposes of drinking water treatment include ensuring the smooth distribution of drinking water while maintaining its aesthetic quality (e.g. taste, odour, colour and hardness) (WHO, 2003) . Meeting the goal of clean, safe drinking water requires a multi-barrier approach that includes: protection of source water from contamination, effective treatment of raw water and safe distribution of treated water to consumer taps. The treatment requirement for potable water supply in rural areas will therefore depend on the quantity of water required, the quantity and quality of the water source. While the design for a small water treatment system varies considerably depending on its application, the majority of these systems were designed following under similar principles (Figure 2.3).

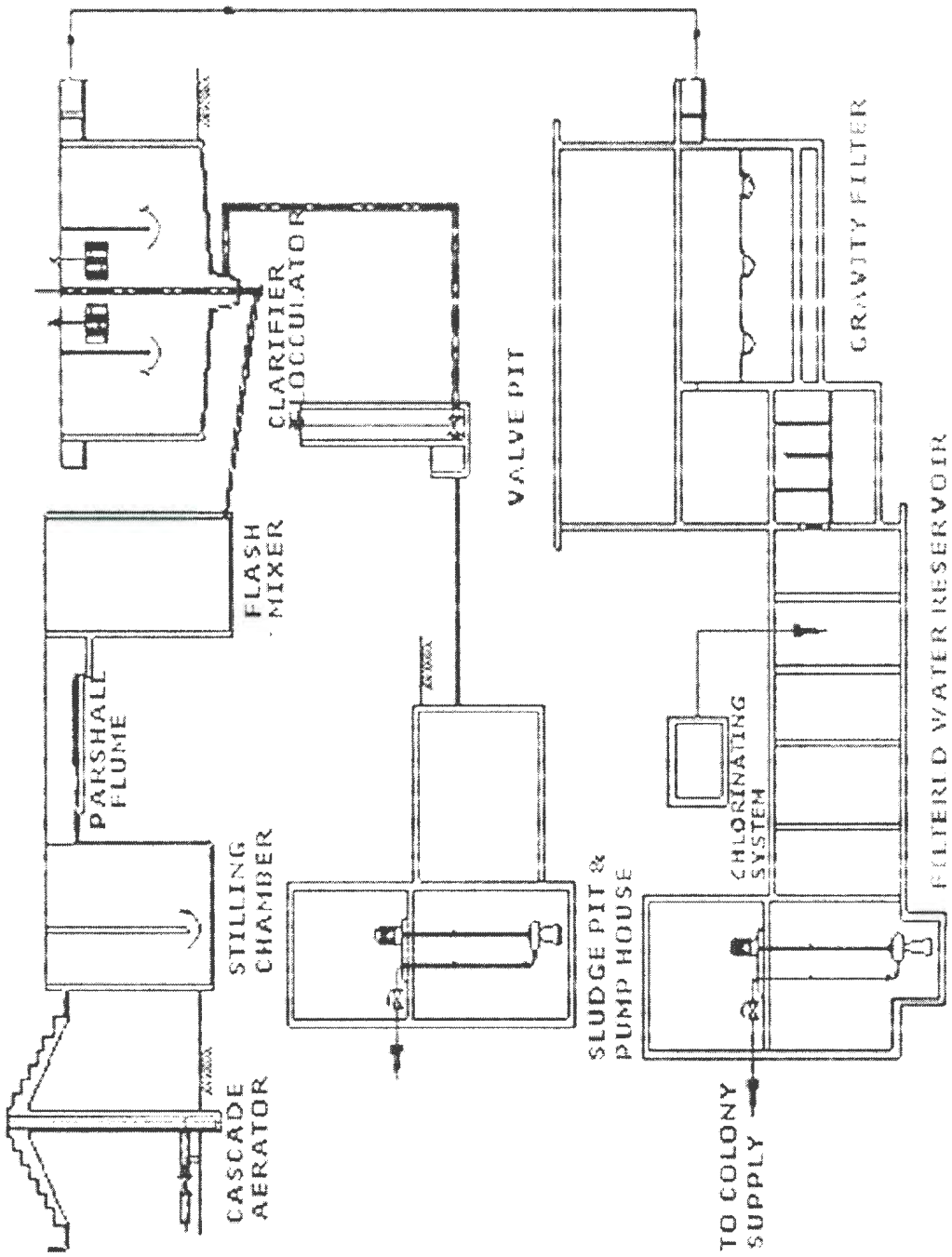


Figure 2.3 The design of a typical potable water treatment plant (Driplexwater, 2012)

2.5 Potable Water Dispensing Units in NL

2.5.1 Development

In order to supply reliable and safe drinking water to rural communities, Fay Environmental Canada Ltd. has developed a small scale water treatment system called the potable water dispensing unit (PWDU). The system can directly take in the water from ambient freshwater sources (e.g., rivers, ponds, and lakes) and efficiently remove most organic and inorganic contaminants and disinfect the water. In terms of operational specifications, the system is specifically suited for drinking water treatment in rural communities given its modest operational and maintenance requirements. The high degree of automation and the use of corrosion resistant materials in the system ensure its minimal operator attendance and durability. Currently, the potable water dispensing unit is being used in a few rural communities in NL, and its configuration is similar to the pilot systems built and operated on numerous raw water sources within Newfoundland (Fay, 2010).

2.5.2 System Configurations

Dependent on raw water quality, the ultimate system configurations will incorporate up to 3 pre-filtration stages (sand filtration, multi-media filtration, and active carbon filtration), ozone oxidation and membrane filtration. As identified on process selection matrix, not all locations will require ozone oxidation, multimedia filtration or softening. However, all locations will incorporate sand pre-filtration, granular activated carbon filtration, membrane filtration (NF or RO) and UV post irradiation is necessary to ensure the water quality prior to dispensing.

Media Filtration is used in PWDU in order to remove suspended matter from water by obstructing its passage with a granular media. As water laden with solids passes through the media, the particles are captured within the filter material. An underdrain beneath the filter bed collects filtered liquid. In a typical filtration bed, the filter media consists of a bed of sand, or a combination of sand and anthracite coal. In a down flow filter arrangement, multi-layer, mixed-grade media allow solids to pass deeper into the bed before collection, resulting in higher filtration rates and longer run lengths before backwashing is necessary. Filtration does not remove dissolved solids.

Activated Carbon is an adsorption media process that involves passing contaminated water through a bed of activated carbon. Adsorption is a natural process by which molecules of a dissolved compound collect on and adhere to the surface of an adsorbent solid. Granular activated carbon is a particularly good adsorbent medium due to its high surface area to volume ratio and its affinity for many organic contaminants. This high surface area permits the accumulation of a large number of contaminant molecules. Granular activated carbon is considered the Best Available Technology (BAT) by the Environmental Protection Agency (EPA) Maximum Contaminant Levels (MCLs) for removing many organic contaminants that exceed maximum.

Reverse Osmosis (RO) is the process by which water, under pressure, is passed through semi-permeable membranes used to remove various soluble inorganics present in the water. The membrane will pass the water, but rejects the dissolved materials to waste. The purified water that passes through the membrane is the permeate or product water. Nanofiltration is a variation of RO with the ability to retain larger ions and pass smaller ions resulting in permeate that is less corrosive to piping. Membrane filtration uses

microporous filters to remove suspended solids, colloidal particles, cysts and bacteria while providing the same high-quality finished water regardless of incoming water turbidity. Contaminants that are smaller than the pore size of the membrane are physically retained and will not pass through the membrane. During normal operation, the membranes are backwashed to sustain optimal performance. In addition to the periodic backwashing, preventative maintenance techniques, such as a short maintenance wash, maximize the time between full chemical cleanings.

Ultraviolet disinfection offers many advantages over other forms of water treatment for microbiological contaminants. Most importantly, it does not introduce any chemicals to the water, it produces no by-products, and it does not alter the taste, pH, or other properties of the water. When used with various forms of filtration, UV light is capable of inactivating microorganisms such as bacteria, viruses, molds, algae, yeast, and protozoa like cryptosporidium and giardia. When used alone, UV light generally has no impact on chlorine, VOCs, heavy metals, and other chemical contaminants.

2.5.3 Field Testing and Implementation

In rural Newfoundland and Labrador, the population is widely dispersed over large areas. Traditionally, people live in those rural areas utilize wells as the main source of drinking water. Although wells provide a bare minimum solution for rural drinking water, the reliability and quality are questionable. For example, due to the lack of effective disinfection, pathogens contained in well water are often known to cause diseases. Consequently, the well water is not even potable before boiled. However, boiling cannot effectively remove the impurities (organic or inorganic) from the well water which is

often marked by unpleasant taste and odour. The presence of some water contaminants may lead to health concerns due to their toxicity and carcinogenicity.

The small scale water treatment system is highly versatile and it can be set up virtually anywhere as long as water is present and the target location is accessible by road. This versatility enables the potential implementation of this system throughout small communities in NF, as most of them are in close proximity to water source and roads. In 2013, as many as 23 PWDU will be distributed at different locations in NF, and 4 of which are currently being tested. However, since the quality of source water varies considerably based on the location in NF, the system operational parameters must be evaluated and optimized based on the local condition.

2.6 Iron and Manganese Removal

High concentrations of iron and manganese negatively affect drinking water quality in several different ways. For example, iron and manganese can react with tannins in coffee, tea, and some alcoholic beverages to produce a black sludge, which affects both taste and appearance. Manganese can be unpleasant in water even when present in smaller concentration than iron. Iron will cause reddish-brown staining of laundry, porcelain, dishes, utensils and even glassware. Manganese acts in a similar way but cause a brownish-black stain. Soaps and detergents do not remove these stains, and use of chlorine bleach and alkaline builders (such as sodium and carbonate) may intensify the stains. In addition, high concentration of iron in water facilitates bacterial growth and excessive iron intake can have detrimental health effects such as chronic iron toxicity due in part to iron accumulation in various organs including the heart, liver, brain, pancreas,

and joints. Many symptoms of iron toxicity are due to displacement by iron of zinc, copper, manganese and other vital nutrients. Metabolic dysfunctions associated with iron toxicity include premature aging, arthritis, birth defects, bleeding gums, cancer, cardiomyopathies, constipation, diabetes, diarrhea, fatigue, headaches, heart failure; hepatitis, hypertension, infections, insomnia, liver disease, mental problems, nausea, parkinson's disease, etc. (Kutsky, R. J., 1981). Excessive manganese intake can causes symptoms mimic those of Parkinson's disease (tremors, stiff muscles) as well as hypertension in patients older than 40. Significant rises in manganese concentrations have been found in patients with severe hepatitis and posthepatic cirrhosis, in dialysis patients and in patients suffering heart attacks. Generally speaking, Symptoms of increased manganese levels include: psychiatric illnesses, mental confusion, impaired memory, loss of appetite, mask-like facial expression and monotonous voice, spastic gait, neurological problems, etc. (Blaurock-Busch, 1997).

Given these negative effects of iron and manganese on drinking water quality, the Canadian drinking water guideline has established standards for iron (0.3 ppm) and manganese (0.05 ppm) in drinking water. These limits are based on aesthetic concerns such as staining, taste and odour. At present, there are no established health standards for either iron or manganese in drinking water in Canada. However, health based standards for these ions should be considered. Taking into account of their known toxicities, the DES Health Risk Assessment Program has adopted an interim health based standard for manganese of 0.84 ppm, and the World Health Organization (WHO) has set up a provisional health-based guideline value of 0.5 ppm for iron.

Currently, the capacity of small scale water treatment systems in terms of iron and

manganese removal remains to be improved. A pilot study in Finland investigated 245 small scale water supplies serving less than 500 individuals in rural areas, high iron and manganese concentrations are among most frequent drinking-water quality problems at 26 percent (WHO, 2011). Also in Finland, another study from the year 2008 suggested that the quality of drinking water produced by small water supplies (N=740) is lower than the quality of water from large water supplies (N=170). The compliance percentages were, however, higher than detected in the pilot study mentioned above. In the category of smallest water supplies, producing 10 to 100 m^3 of water per day, 97% of the results complied with the quality requirements for total coliforms; the corresponding percentage was 99.4% in the category of the largest water supplies, producing over 1000 m^3 of water per day (WHO., 2011).

According to the water quality assessment conducted in Newfoundland, iron and manganese are among the most abundant water impurities in the region. Therefore, this nature of the ground water in Newfoundland made it crucial to evaluate the iron and manganese removal capacities of small scale drinking water treatments systems serving the region.

Oxidization of iron and manganese convert ferrous ions (Fe^{2+}) iron to ferric state (Fe^{3+}) and (Mn^{2+}) to (Mn^{4+}) state, the oxidized salts will precipitate as ferric hydroxide and manganese oxide, that to reach the concentrations of these pollutants under their limit values in drinking water (El Araby et al., 2009). For this purpose, ozone is often used as the oxidizing agent given it superiority over other methods such as aeration or chlorine. Oxidation of iron by aeration is also possible unless the iron is complexed or the reaction has to take place under acidic conditions. Manganese, complexed or not, cannot

be oxidized by aeration. Chlorine can also be used for oxidation of iron and manganese, but it is less effective than ozone as more chlorine is required than ozone for equal degree of oxidation. This is due to the fact that ozone has an oxidation potential 150% greater than chlorine. The use of chlorine can also result in the formation of THM if organic material is present in the water. Ozone is evidently the strongest oxidant and chemical disinfectant available commercially, and it is used by the more than 3,000 plants throughout the world. However, the adequate application of ozone requires a rather complex engineered subsystem, e.g., the ozone generator, feed gas treatment, power supply, and the removal of iron and manganese using ozone are governed variety of factors.

2.7 Design of Experiments Method

Design of experiments (DOE) aims to investigate systems and process to obtain maximum amount of information with minimum input resources. DOE can be divided into three categories, namely one-factor-at-a-time-method (OFAT), factorial experimental design, and orthogonal array. A schematic diagram showing relationship between different approaches with the design of experiment is shown in Figure 2.4. The OFAT and factorial experimental design both essentially analyze all possible combination of levels/factors, with factorial experimental design being able to evaluate the possible interactions of several factors. In this study, given the large amount of time and resource required to conduct each run, and large number of factors/levels combinations, it is impractical to use either OFAT or factorial design approach to design the experiment. In order to conduct the experiment efficiently, experiment runs that potentially generate

redundant data must be avoided. Therefore, the orthogonal array approach was selected as it focuses on the contrasts that are represented by vectors and sets of orthogonal contrasts are uncorrelated and independently distributed if the data are normal. Because of this independence, each experimental run with a certain factor/level combination will generate novel information comparing to others. Within the orthogonal array methods, the central composite design method is the most suitable for the factors analyzed in this study as the factors potentially affecting iron and manganese removal efficiencies are somewhat independent of each other. This relationship among the factor analyzed exclude the mixture experiments as it requires a proportional relationship among factors. On the other hand, the taguchi method is more frequently used to streamline a series of operations.

As this research aims to evaluate the effect of various factors on the performance a SWTP in removal of iron and manganese, a second order model for the response variable (removal efficiency) need to be established without using a complete three-level factorial experiment. Therefore, the review of this research will focus on the Central Composite Design (CCD) as it is the most relevant approach to our objectives. CCD is a type of orthogonal array design approach that seeks to establish a second order model for the response variable without using a complete factorial experiment, that is distinct from Taguchi method (involving loss functions) and mixture experiment (independent factors are components with addition constraints). A CCD consists of three groups of design points: 1) two-level factorial or fractional design points; 2) axial points (star points); and 3) center points (Montgomery, 2008).

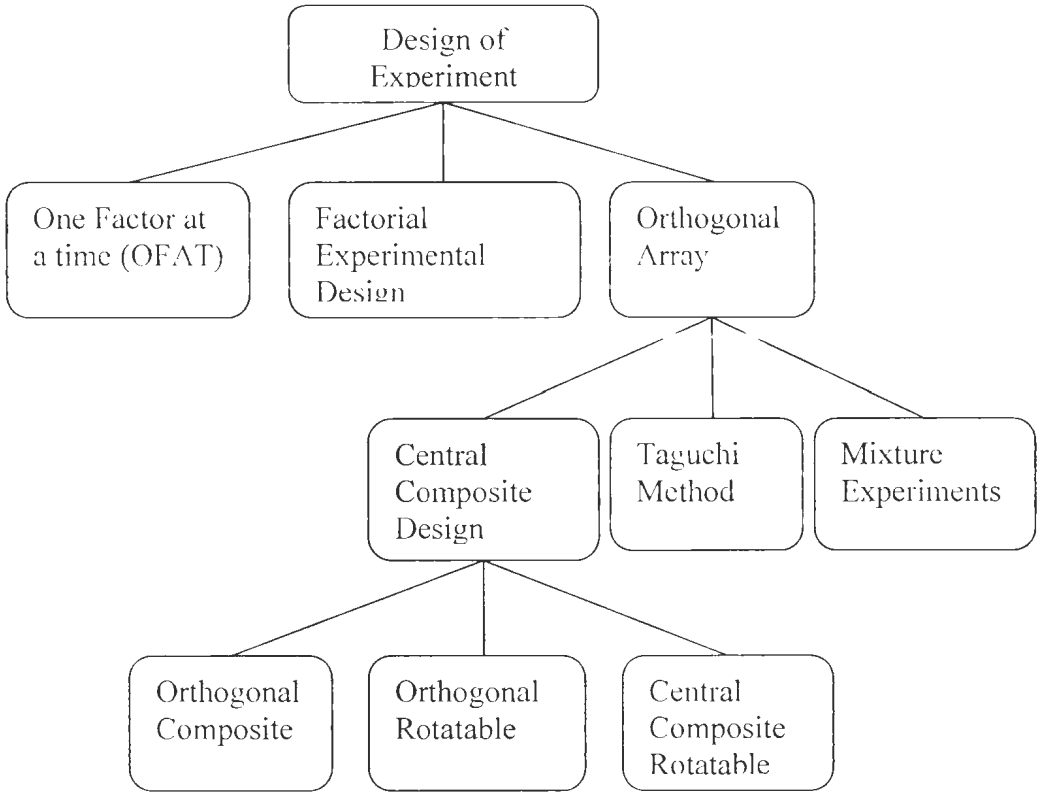


Figure 2.4 The overall view of design of experiment

2.8 Summary

Access to safe drinking water is not only fundamental to good health but also to satisfactory livelihoods, dignity and prospects for economic growth and education. The lack of access to sufficient amounts of safe water leads to human suffering and to loss of human potential, which is ethically indefensible as well as economically wasteful. Safe and acceptable water for human consumption that is available in sufficient quantity, physically accessible and affordable is a crucial requirement for human wellbeing. In terms of drinking water supply, it is often not feasible and cost-efficient to construct large- or medium-scale water treatment plants or connect the small and sparse

communities to existing facilities. Small scale water supplies play important roles of water supply in rural areas and its application in NF will significantly improve the drinking water quality for small communities in the region. However, since the environmental condition varies among different potential sites, the operational parameters must be evaluated and optimized to improve the effectiveness of these systems across Newfoundland.

In Newfoundland, small drinking water treatment plants are generally capable of producing water that meets the drinking water standards but many of these facilities face technical challenges in the removal of colour which occasionally presents in the treated water. Previous studies have indicated that relatively high levels of iron chelates and complexes (e.g., $\geq$ 200 µg/L) and/or manganese (e.g., $\geq$ 150 µg/L) combined with colour values of 100 mg/L PtCo equivalent or greater would cause particular difficulties in treating the water (FECL, 2009). The above challenges are not only being faced by the PWDU, but are also especially faced by most of the small scale water treatment systems in the market or under research. Therefore, it is important to conduct laboratory experiment aimed to enhance the removal of iron and manganese ions to eradicate the color present in water treated by small water treatment plants. In addition, this research could also help us to gain more knowledge in improving the manganese and iron removal in drinking water treatment.

CHAPTER 3 MATERIALS AND METHODS

3.1 Performance Evaluation

In comparison to large scale drinking water treatment systems, SWTPs are often more prone to technical difficulties due to their compactness and variable working environment in which they operate. In order to identify and prevent such technical difficulties, performance evaluations including a number of following components are often needed:

a) Monitoring of the water quality (e.g., temperature, turbidity, alkalinity, pH, hardness, iron, manganese, and TOC) following each of the treatment units and stages under regular operation conditions (e.g. parameters at default settings);

b) Monitoring of the variations in quality of raw water and treated water due to accidental operational and environmental changes (e.g., inflow/outflow rates and timing of backwash; quality and quantity changes in pond water caused by precipitation and seasonal recharges) in order to assess the robustness of this system.

c) Evaluation of the system performance under various operational parameters;

d) Development of an operation database system to support optimal operation and further design and refinement of the system.

However, from a practical point of view, it is hard to design an experiment that is comprehensive enough to address all the above components. Therefore, it usually needs to identify the most urgent challenges a specific that SWTP may face in a given working environment and time.

Iron and manganese are among the most abundant ions in the fresh water systems of rural Newfoundland. At high concentrations, the ion complexes (e.g., ≥ 200 µg/L for iron and ≥ 150 µg/L for manganese) result in the presence of color in water(FECL, 2009). Although small drinking water treatment plants are generally capable of producing water that meets the drinking water standards, many of these facilities face technical challenges in the removal of colour in treated water possibly due to the presence of high levels of residual iron and manganese ions.

This nature of raw water in rural Newfoundland and the technical challenge this brings upon the SWTPs serving this region made the removal of iron and manganese the top priority among the aspects of SWTPs that need to be evaluated and improved. Therefore, the iron and manganese were selected as experimental parameters with influent concentration ranges tailored to reflect natural variations among different locations in Newfoundland (Figure 3.4 and 3.5). The concentrations of these ions in the effluent were also monitored to determine the removal efficiencies at varying conditions. Although in theory that there are several operational parameters in the SWTP can potentially influence treatment performance, in reality, flow rate and ozone dosage are the most accessible parameters to the operator which also have the highest likelihood of affecting the system performance. In addition, these parameters are also easily gauged and monitored by the operator from the control panel, making them the ideal parameters for experimental testing.

3.2 Experimental Methods

3.2.1 Preparation of Influent

Although this current study aims to test system performance using influent with varying qualities from Newfoundland locations, it is neither feasible to collect and transport water samples from various locations to the testing location given the large of volume of water required for each test (~680 L), nor it is feasible to conduct tests at various locations given the large amount of efforts involved in setting up the system at any given location and the limitation of sites that can serve as testing locations (e.g. the site permission and accessibility as well as the limited funds and time). Therefore, the synthetic water influent used in this study was produced based on the iron and manganese concentrations of samples collected from typical freshwater sources in Newfoundland (See section 3.3.3 for details). Based on the data from these surveys, the iron and manganese concentrations in Newfoundland freshwater systems typically ranges from 0.25 - 1.2 mg/L and 0.02 - 0.8 mg/L, respectively. In addition, it has been previously shown that high levels of iron and manganese are associated with the colour that is occasionally present in the treated water (FECL, 2009). Since previous reports have shown that relatively high levels of iron chelates and complexes (e.g., $\geq$ 200 µg/L) and/or manganese (e.g., $\geq$ 150 µg/L) combined with colour values of 100 mg/L PtCo equivalent or greater would cause particular difficulties in water treatment (FECL, 2009). In this study, influent water samples with target iron and manganese concentrations were produced by dilution of standard $FeCL_2$ (1M, Fisher Scientific) and $MnSO_4$ solutions (1M,

Fisher Scientific). Tap water was used for producing synthetic influent in order to avoid the influence of other impurities in the raw water from the ambient water bodies.

3.2.2 Operational Procedures

In this study, the experiments were carried out by using a PWDU system shown in Figure 3.2. In the PWDU, (see Figure 3.4 for the conceptual design and Figure 3.5 for a picture of the actual system), influent water enters through a mono-media sand filter (TK1) where gross particulate and macroscopic organic matters are removed. The filtrate is leaving the sand filter and mixed with an ozonated stream coming from downstream of the ozone reactor vessel or provided via a recirculation loop between the sand filter and reactor vessel (TK2). In either case, water is supplied by a vertical multistage pump which causes a pressure drop across a venture style injector, creating a vacuum to inject generated ozone under sub-atmospheric pressure. Ozone is supplied to the process stream on-demand by a corona discharge type ozone generator and the applied dose can be adjusted on the generator's control panel. Within the generator housing, a small air compressor forces ambient air through an oxygen concentrator, which separates the various constituents (i.e., nitrogen and oxygen) in the air by their physical size. Consequently, oxygen with a high purity (90~96%) is generated for the conversion into ozone while other constituents in the air (mostly nitrogen) are vented harmlessly to atmosphere. The corona discharge method of ozone generation works by subjecting an electrode to a high electric potential which ionizes the purified oxygen supplied to the generator. These oxygen ions are then recombined to form primarily ozone molecules, and are drawn by vacuum through the venturi. This style of ozone generation is superior

to UV ozone generation given its lower electrical energy requirement and gas volumes produced.

Under the bombardment by high-speed charged particle formed under accelerating of high frequency high voltage electric field, the bond between oxygen atoms in an oxygen molecule breaks, giving rise to two oxygen atoms ($e+O_2 \rightarrow 2O+e$). Subsequently, the oxygen atoms collide with remaining oxygen molecules, producing ozone molecules. ($O+O_2+M \rightarrow O_3+M$; $O+O_2+M \rightarrow O_3+M$).

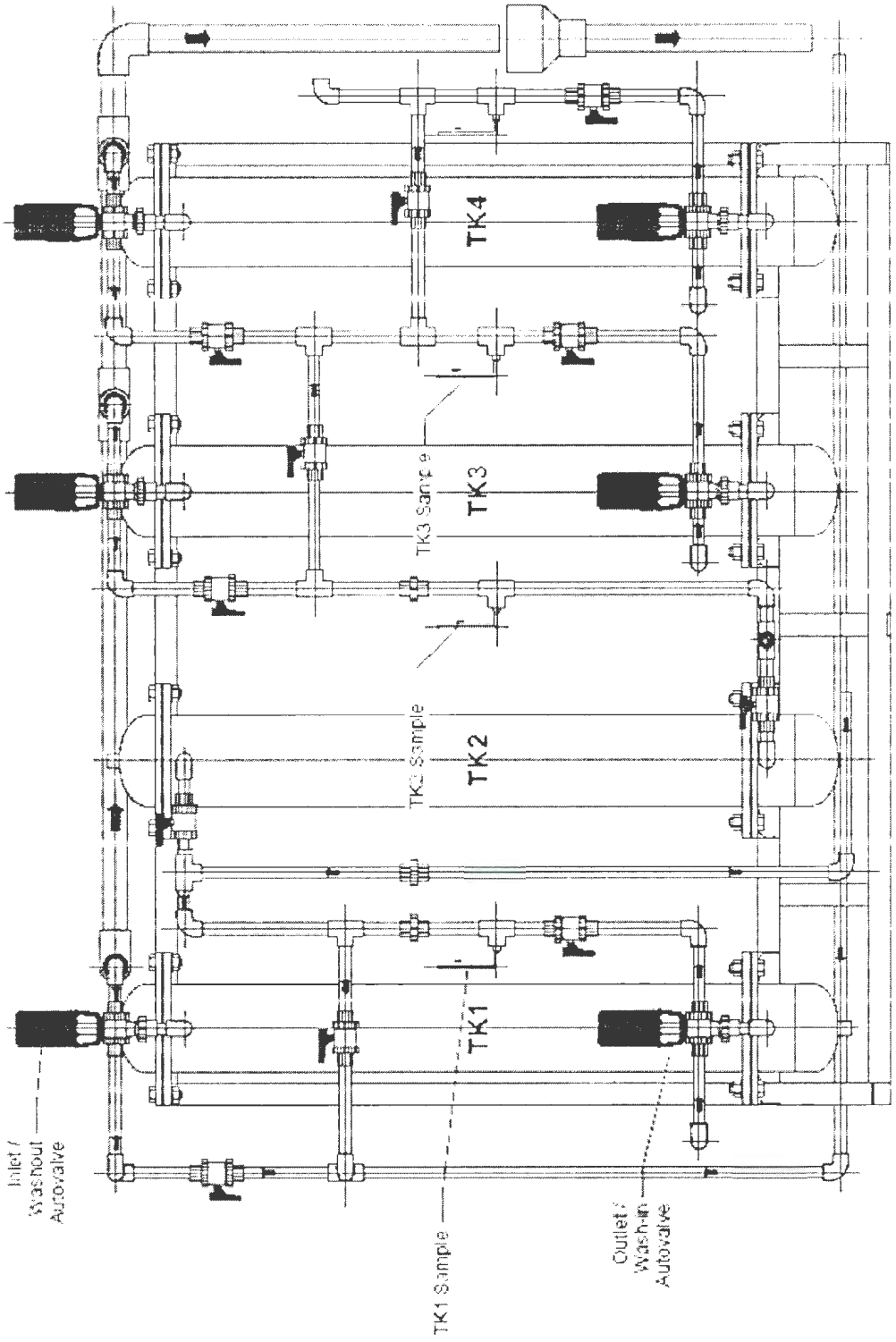


Figure 3.1 Layout of the PWDU pilot testing in Newfoundland (FECL, 2009)
TK1-Sand filter TK2-Ozone TK3 Multi-media filter TK4-Granular activated carbon filter

Once ozonated, water is forced into the ozone reactor vessel by jet, promoting further mixing of ozone in the process stream. Both the ozone reactor vessel and the multimedia filter (TK3) are fitted with gas release valves piped directly to a catalytic ozone destructor containing a permanganate media that completely reduces or binds to all vented ozone. Ozone within the process stream is allowed sufficient contact time to physically destroy pathogens within the water and reduce metal chelates and organic compounds. The entire process stream and venting system is comprised of materials suitable for indefinite contact with wet ozone. Products of chemical reduction are largely removed from the water in the sand/anthracite multimedia filter following the ozone reactor vessel, and then polished using a granular activated carbon (GAC) adsorptive media (TK4).

The treated water flow rate is monitored and totalized via a pulsed-head paddle type flow meter. The treated water is stored in a 1,000L capacity stainless steel storage tank. This tank is fabricated as part of the process skid to make best use of available space and minimize the skid footprint. This storage tank features a sloping floor angled toward the pumped end of the base, which ensures that the tank can be fully drained if needed. Flow rate is adjusted using a through-pattern needle valve. Total and instantaneous flow are displayed locally on a digital panel and exported via modem for centralized monitoring from the Fay offices in St. John's, NL. Tank water level is monitored using a pressure level transducer communicating continuously with the SCADA system. When the storage tank water level drops below 60% of its capacity, a signal is sent to start the forward feed and membrane pumps. The system then begins to produce treated water.

Treated water is then pumped to the dispensing station (provided by others) under hydropneumatic pressure. This pressure is generated via a booster pump which charges a small hydropneumatic vessel, and is controlled with a pressure switch. This configuration allows for regular usage of the taps without constantly energizing and deenergizing the booster.

Backwashing of each filter is performed using treated water to prevent nozzle clogging and biofouling of filter media, and is initiated after a pre-determined operating time. When a wash sequence is initiated, the 3 way automatic L port valves on top of each vessel are toggled to backwash service and the vessel is depressurized. A volume of water equal to roughly 2.5 – 4 media bed volume flows through the filter via the backwash and recirculation pump, fluidizing the media and washing entrained particulate such as reduced metals and organic matter which have accumulated during service to drain. Combined water / air scour is used during daily backwashing of the inlet sand filter to aid in the breakup of compacted media. Separate water / air scour is used on the multimedia filter; this is done to preserve the anthracite layer. The rigor of a combined wash has the effect of lifting and washing out the anthracite media, reducing its volume over time and ultimately its useful life. Air scour is not utilized for cleaning GAC as it can pulverize the media thereby decreasing its efficiency. Backwash flow is monitored using a variable area rotameter with automatic low flow indication. As each filter requires differing wash rates, individual through-pattern flow control valves shall be provided on each filter backwash line to regulate the flow.

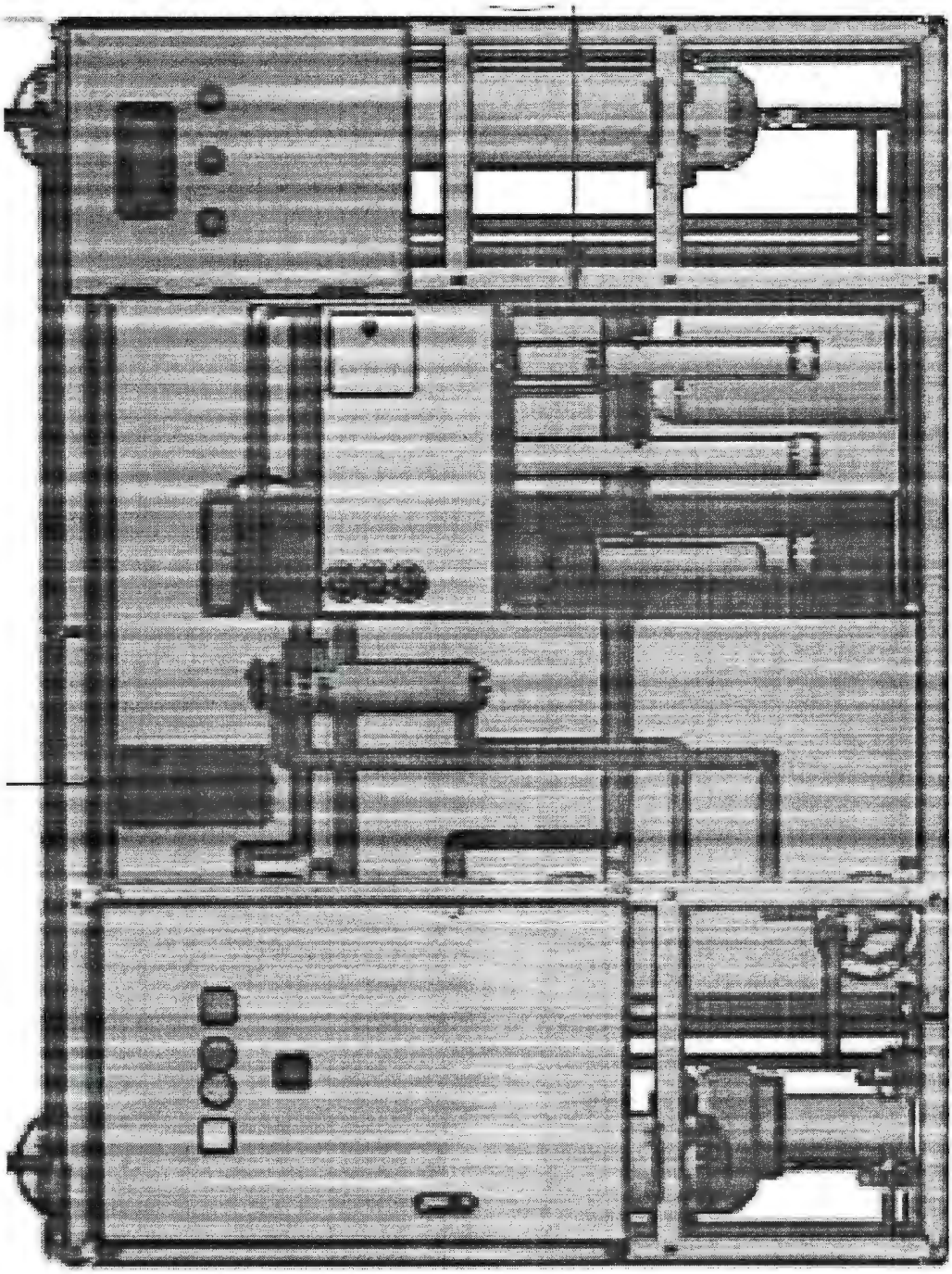


Figure 3.2 The Conceptual Layout of PWDU (FECL, 2010)

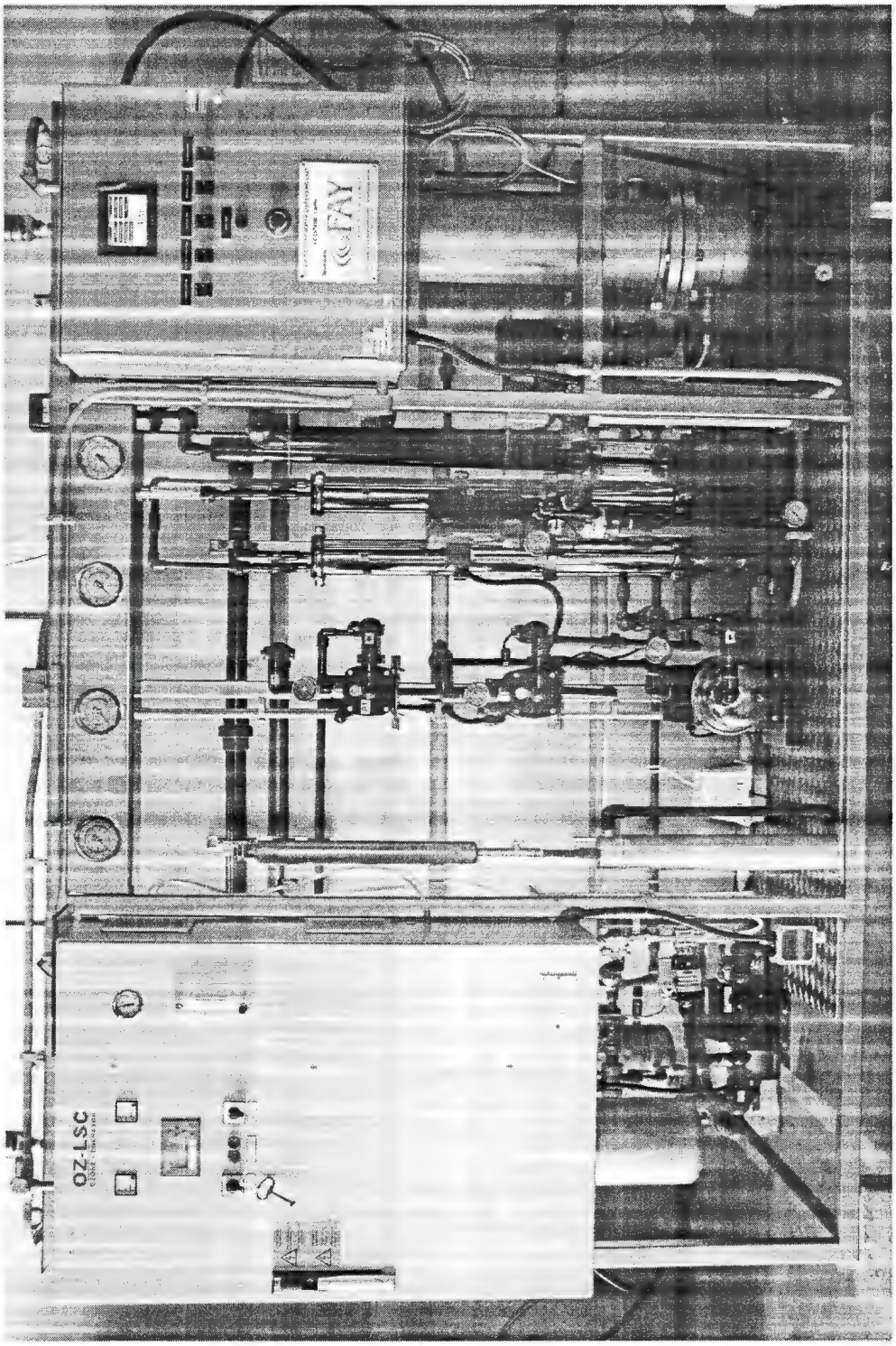


Figure 3.3 Potable water dispensing unit 2012

3.2.3 Sampling Scheme

Since more than one testing runs were usually performed consecutively on a given day, it is important to ensure that the samples were only collected after when a previous run had elapsed (i.e., the effluent from the previous run left the system completely) to avoid influence of results by preceding run. Given that the total circulation volume of the PWDU system is known (0.22 m^3), thus the processing time for each run can be calculated as the ratio of the circulation volume to the flow rate. The processing time guides the sampling scheme in which samples were only collected after processing time had elapsed. This sample scheme was followed throughout the study.

3.2.4 Sample Collection and Preservation

In this study, the effluent and raw water samples were collected in 40 ml glass bottles. To prevent precipitation of salts, water samples were preserved with nitric acid to pH less than or equal to 2 immediately after collection. All samples were refrigerated at 4°C (±2°C) from the time of collection until digestion for analysis. To determine if the sample collection, transport, storage, and preservation procedures had influenced the water quality results, a field reagent blank (FRB) sample consisted of distilled water (i.e., the method blank) was also collected, transported, stored, and preserved in the same manner as the actual experimental samples. This FRB sample was also subjected to water quality assessment to determine if the experimental procedures had any impact on water quality (e.g. contamination).

3.2.5 Sample Analysis

3.2.5.1 ICP-MS

The water quality analysis in this study was conducted using HP 4500 plus ICP-MS equipped with a quadrupole mass filter, hosted by CREATI lab at Memorial University of Newfoundland. ICP-MS is a highly sensitive analytical tool capable of determining a wide range of elements at low concentrations, usually below one ppb (depending on the element to be determined and sensitivity of the instrument). It is generally used to detect positive ions while negative ions (halognes) are also produced in the plasma (Thomas, 2001).

An ICP-MS combines the principles of inductively coupled plasma with a mass spectrometer. An inductively coupled plasma creates plasma, which is in a gas-like phase that contains enough ions and free electrons to make the vapour phase fluid electrically conductive. Mass spectrometry separates ions formed in the plasma according to their mass/charge ratio. Then a signal, proportional to the concentration of the analyte, is detected, which leads to the determination of elemental concentrations. In general, argon is the gas of preference to create the plasma due to its natural abundance that translates to a lower cost compared to other noble gases. The signal produced by the sample, is compared with the ion signal of a reference standard material that is produced during the calibration of ICP-MS. This allows the determination of the concentration of the elements (Thomas, 2001). In this study, all procedures involving ICP-MS followed HP 4500 ChemStation Operator's Manual.

3.2.5.2 Water Sample Quality Analysis

Prior to the analysis of the samples involved in this study, the method detection limit was determined to ensure the analytical performance of the instrument is consistent (i.e. not affected by either a change in instrument hardware or operating conditions). The method detection limit (MDL) is defined as the minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero. In this study, the MDL was established for all wavelengths utilized, using reagent water (blank) fortified at a concentration of two to three times the estimated instrument detection limit. The MDL values were determined based on the analysis of seven replicate aliquots of the fortified reagent water and process through the entire analytical method. The MDL values were calculated using the following equation:

$$M = t \times S$$

Where:

t = students' t value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom

S = standard deviation of the replicate analyses

Before each of the ICP-MS analysis, standard calibrations were performed with 10 technical replicates. In the ICP-MS analysis involved in this study, the instrument detection limit was defined as the concentration equivalent to the analyte signal which is equal to three times the standard deviation of a series of 10 replicate measurements of the calibration blank signal at the same wavelength. As part of the standard calibrations, a

quality control sample (QCS) was also included in the analysis to check both laboratory or instrument performance.

For every ICP-MS run, a laboratory fortified blank (LFB) was prepared by fortifying an aliquot of the laboratory reagent blank with all analytes to a concentration approximately 100 times their respective MDL. The LFB was then taken through all the preparation procedures prior to ICP-MS analysis to determine if these preparation procedures had influenced the results. In addition to the LFB, a laboratory reagent blank (LRB) was also included in each analysis run to determine if there are any analytes interferences present in the laboratory environment, reagents, or apparatus. An instrument performance check (IPC) solution was also used to verify instrument performance during analysis. At the end of every ICP-MS run, the last sample was analyzed twice to ensure that the technical variability in water quality assessment did not significantly affect the results. Following each of the samples analyzed, a rinse blank consists of acidifying reagent water (same concentrations of acids as used in the calibration blank) was used to flush the system to reduce memory effects.

In this study, the treated water samples of all experimental runs were preserved for analysis by ICP-MS. Given the large amount of water that is required for water treatment runs, the tap water from the municipal treatment facilities was the only realistic option as source water. However, the tap water used likely contained an acceptable level of impurities including iron and manganese (referred to as "background concentrations" hereafter). In order to account for background concentrations, a total of 10 tap water samples were taken and subjected to ICP-MS analysis. The average concentrations of iron

and manganese were calculated and accounted for in subsequent analysis (e.g. removal efficiency).

3.2.6 Calculation of Removal Efficiencies

In this study, the removal efficiencies for iron and manganese were defined as the proportion of iron and manganese that were removed after the treatment, which were calculated using the following function:

$$R = \frac{CIC + BC - EC}{CIC + BC} \times 100\% \quad (3.1)$$

R: Removal efficiency of iron or manganese in percentage (%);

CIC: Calculated influent concentration of iron or manganese (mg/l);

BC: Background concentration of iron or manganese (mg/L); and

EC: Effluent concentration of iron or manganese

The calculated influent concentrations were based on the amount of iron and manganese added to achieve target concentrations. The concentration of iron and manganese in tap water were randomly sampled at 10 different occasions throughout the testing period (i.e., background concentration), and the actual influent concentration was estimated by addition of average background concentrations (i.e. BC in the Equation 3.1) to the calculated influent concentrations (i.e., CIC in the Equation 3.1) of iron and manganese. The amount of iron and manganese removed was then calculated by subtracting effluent concentrations (measure by ICP-MS) from the estimated actual influent concentrations.

3.3 Experimental Design

In evaluating system performance and influence of environment and operating conditions, there are several potential parameters (e.g. influent concentrations, flow rate, and ozone dose) that might be considered, and each of which can be set at multiple levels. The number of possible combinations between various parameters and levels are too numerous (i.e. the product of number of levels for all parameters) to be tested. Therefore, the experimental design needs to be streamlined in order to reduce the scale of the experiment while maintaining its potential to provide information that yield to valid conclusions. Design of Experiments (DOE) has portrayed a major contribution in science and technology since the time Sir Ronald Aylmer Fisher introduced this concept in the 1940s (Belavendram, 2011). The concept of experimental design is to yield the most information from the fewest runs of an experiment. By applying experimental designs in a pilot test, the time and cost could dramatically be reduced. Besides, such approach would also lead the processes and products to get better performance and achieve greater reliability.

3.3.1 Response Surface Method

The objective of this study is to determine the effects of flow rate, ozone dose, and influent iron and manganese concentrations on iron and manganese removal efficiencies. In order to achieve these objectives, the experimental design needs to account for these factors and their interactions. Without using a complete three-level factorial experiment, the response surface method can establish a second order model for the response variable (i.e. removal efficiency of iron and manganese) that helps to assess the effects of these

factors and interactions on the removal of iron and manganese by SWTP. A CCD has three groups of design points: a) two-level factorial or fractional design points, b) axial/start points and c) center points. CCD's are designed to estimate the coefficient of a quadratic model. All point descriptions will be in terms of coded values of the factors. CCD Response surface methodology (RSM) based on central composite design (CCD) with five levels was used to generate prediction models. This method can greatly reduce the number of required runs (from 500 to 80 runs), and is powerful in determining the interaction between factors.

CCD in this research was carried out in blocks. Blocking is advantageous when all of the experiments cannot be carried out in one day or with one batch of material. The factorial points can be divided in such a way that the blocked effect is eliminated before computation of the model. The first one or more blocks consists of the factorial design with some center points. The remaining block consists of the star points with additional center points.

3.3.2 Selection of Parameters

Using Design-Expert v8.0® (Stat-Ease, Minneapolis, MN), a module considering four independent factors was employed to evaluate the removal efficiencies of iron and manganese removal by the PWDU under varying operating conditions. Although it is known that the removal efficiencies for iron and manganese are subjected to influences by many other factors including filter composition, the flow rate and ozone dosage both play a major role in governing the removal efficiencies of these ions and are easily manipulated during a treatment operation. Therefore, aimed to improve operational

parameters at varying influent iron and manganese concentrations, flow rate, ozone dosage, influent iron concentration, and influent manganese concentration were chosen for testing in this study.

3.3.3 Determination of Levels and Categories

With exception of ozone dosage, which can only be set at 4 different levels in the ozone generator (OZ9-LSC, see Tale 3.1 for more details), 5 levels were chosen for the rest of parameters given the minimum and maximum values. The range of flow rate used for testing level determination by the Design-expert 8.0 software was same as the recommended range specified in the PWDU manual. A total of 80 treatment runs with each run representing a unique combination of levels for the 4 parameters were generated by the Design-Expert 8.0 software.

In order to determine testing levels for influent iron and manganese concentrations, prevailing water quality in Newfoundland freshwater systems were taken into the account when generate testing levels. The ranges of iron and manganese concentrations in Newfoundland were estimated based on results from a previous survey conducted by Fay Environmental. In this survey, a total of 37 sites were visited (See footnotes of Figure 3.4 for complete names of all sites) and water samples were taken and subjected to ICP-MS analysis. For each site, the average and maximum concentrations for iron (Figure 3.4) and manganese (Figure 3.5) were reported. Based on the concentration results, the concentration average ranges for iron and manganese were 0.23 to 1.17 mg/l, and 0.02 to 0.71mg/l, respectively.

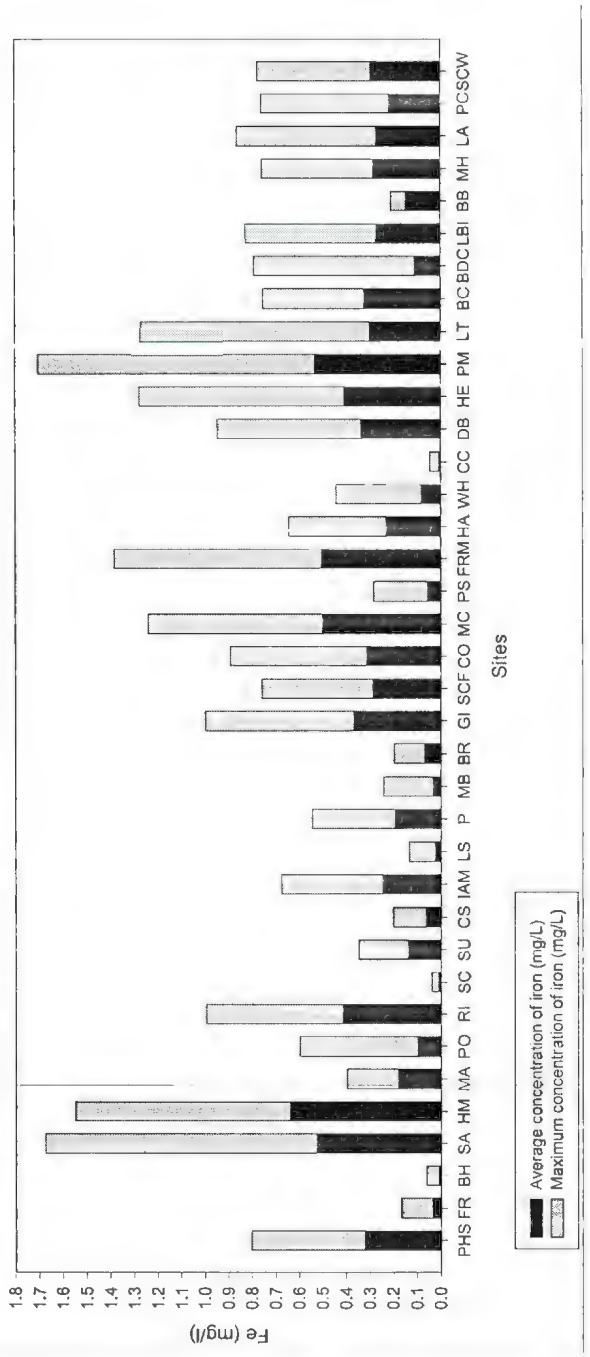


Figure 3.4 The concentration of iron at various Newfoundland locations* *Bunyan's Cove (BC), Hermitage (HM), Isle aux Morts (IAM), Lawn (LA), Point May (PM), Pool's Cove (PC), Deadman's Bay (DB), La Scie (LS), Ming's Bight (MB), Salvage (SA), Seal Cove (SC), Fox Roost Margaree (FRM), Leading Tickles (LT), Makkovik (MA), Mary's Harbor (MH), Port Hope Simpson (PHS), Port Saunders (PS), Postville (PO), Rigolet (RI), Sheaves Cove (SHC), Conche (CO), Whiteway (WH), Baine Harbour (BH), Happy Adventure (HA), Harbour Mille (HM), Chance Cove (CC), Sunnyside (SU), Francois (FR), McCallum (MC), Birchy Bay (BB), Brighton (BR), Cottlesville (CO), Pacquet (PA), Black Duck Cove (BDC), Gillams (GI), Little Bay Islands (LBI)

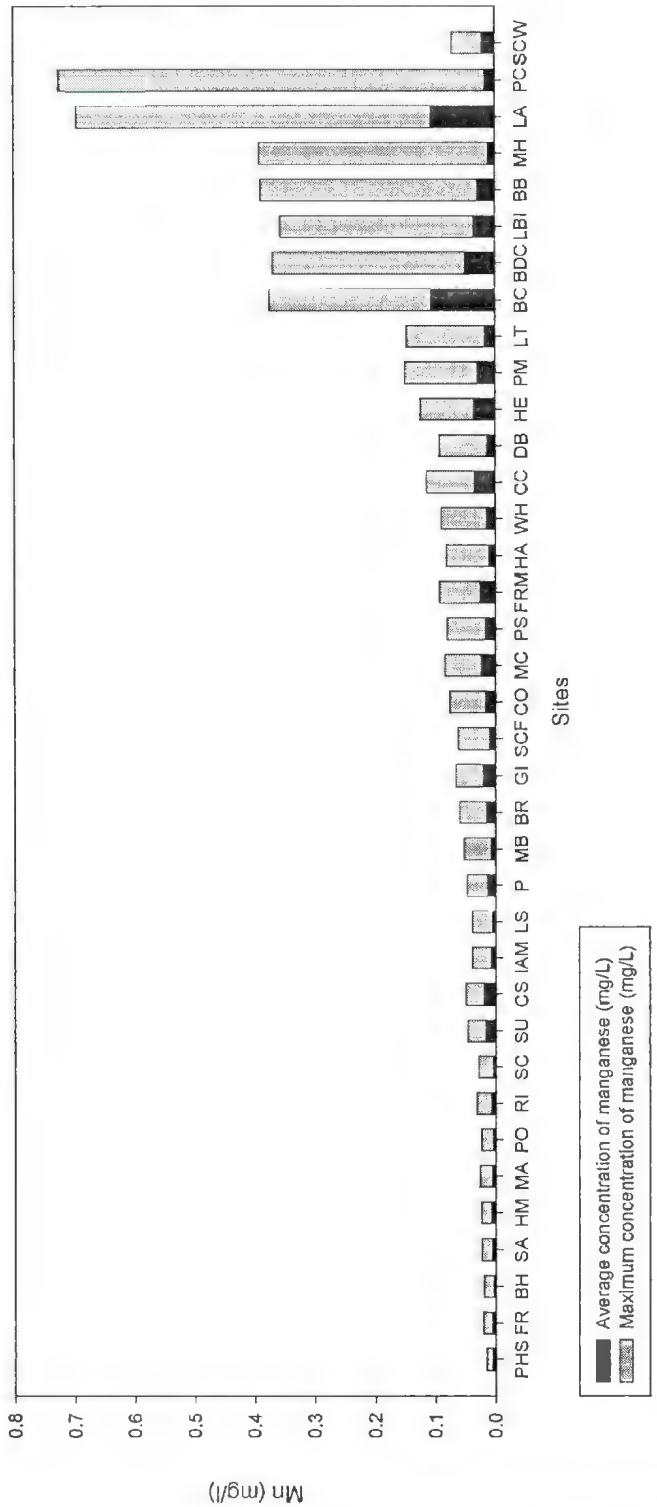


Figure 3.5 concentration of manganese at various locations (see Figure 3.4 for full names of all locations).

The ozone generator (model No. OZ9-LSC) used in the PWDU is manufactured by Kaufmann Umwelttechnik in Germany. This generator has a maximum output capacity of 10 g/hr. This ozone production capacity translates to approximately 22.5 mg/L or 6% ozone concentration at the maximum flow rate of 444 L/hr. Not only has this concentration satisfied the 10 mg/L dosage requirement in the specification, it is also above the 20 mg/L ozone dosage requirement to account for variations in raw water qualities as determined based on the internal test results obtained by Fay Environmental (data not shown). Therefore, this ozone generator satisfies the operational requirement of the PWDU, and it is built into the system. The OZ9-LSC generator is a Corona discharge type ozone generator that uses water for cooling. The ozone production level of this system is controlled by a 4-step switch that directly controls the voltage of the discharge, which translates to 4 different levels of ozone production (Table 3.2) as well as the 4 levels used in CCD.

Table 3.1 Ozone dosage parameters settings

Switch	Voltage of discharge (KV)	Ozone production (g/hr)
Step 1	6	4.0
Step 2	8	7.0
Step 3	9	8.5
Step 4	10.2	10.0

3.3.4 Central Composite Design

Response surface methodology (RSM) based on central composite design (CCD) with five levels were used to generate the prediction model as the RSM method can greatly reduce the number of required runs (from ~500 to 80 runs), and it is powerful in determining the interaction between factors. RSM is a collection of mathematical and

statistical techniques that are useful for the modelling and analysis of problems in which a response of interest is influenced by several variables and the objective is to optimise this response (Montgomery, 2008). RSM also quantifies relationships among one or more measured responses and the vital input factors (Design-Expert Software, 2012). It was mentioned previously that RSM designs also help in quantifying the relationships between one or more measured responses and the vital input factors. In order to determine if relationship exists between the factors and the response variables investigated, the data collected can be analyzed using regression to describe the data collected whereby an observed, empirical variable (response) is approximated based on a functional relationship between the estimated variable, y and one or more regressor or input variable $x_1, x_2, \ldots, x_i$. In the case where a non-linear relationship exists between a particular response and three input variables, the following quadratic equation: may be used to describe the functional relationship between the estimated variable, y and the input variables x_1, x_2 and x_3.

$$y = b_0 + b_1 \cdot x_1 + b_2 \cdot x_2 + b_3 \cdot x_3 + b_4 \cdot x_1 \cdot x_2 + b_5 \cdot x_1 \cdot x_3 + b_6 \cdot x_2 \cdot x_3 + b_7 \cdot x_{21} + b_8 \cdot x_{22} + b_9 \cdot x_{23} + error \quad (3.2)$$

The least square techniqueis being used to fit a model equation containing the said regressors or input variables by minimising the residual error measured by the sum of square deviations between the actual and the estimated responses. This involves the calculation of estimates for the regression coefficients, i.e., thecoefficients of the model variables including the intercept or constant term. The calculated coefficients or the model equation need to however be tested for statistical significance. In this respect, the the following test were preformed.

The version 8 of the Design Expert software was used to develop the experimental plan for RSM. Numerical Factors including initial iron concentration (0.25, 0.44, 0.73, 1.01 and 1.20 mg/L), initial manganese concentration (0.02, 0.18, 0.41, 0.64 and 0.80 mg/L), flow rate (200, 261, 350, 439 and 500 L/hr), and one 4 level categorical factor ozone dose (4, 7, 8.5 and 10 g/L, respectively) were analyzed through a 80-run CCD design. The response that was used as target optimization functions are concentrations of manganese and iron of the effluents which were quantified using ICP-MS. The values of independent variables were founded (Table 3.3).

Table 3.2 Uncoded and coded levels of the independent variables used in the RSM design

Symbols	Independent variables	Code levels				
		-alpha	Low	0	high	+alpha
A	Flow Rate l/h	200.00	260.80	350.00	439.19	500.00
B	Conc. Mn mg/l	0.02	0.18	0.41	0.64	0.80
C	Conc. Fe mg/l	0.25	0.44	0.73	1.01	1.20

Table 3.3 Response surface central composite design

Std No.	Run	Block	Factor 1 A:Flow Rate (l/hr)	Factor 2 B:Conc. Mn (mg/l)	Factor 3 C:Conc. Fe (mg/l)	Factor 4 D:Ozone Dose (g/hr)
69	1	Block 1	350	0.4	0.7	10
1	2	Block 1	261	0.2	0.4	4
26	3	Block 1	439	0.2	1.0	7
4	4	Block 1	439	0.6	0.4	4
7	5	Block 1	261	0.6	1.0	4
6	6	Block 1	439	0.2	1.0	4
41	7	Block 1	261	0.2	0.4	8.5
70	8	Block 1	350	0.4	0.7	10
64	9	Block 1	439	0.6	0.4	10
10	10	Block 1	350	0.4	0.7	4
30	11	Block 1	350	0.4	0.7	7
27	12	Block 1	261	0.6	1.0	7
21	13	Block 1	261	0.2	0.4	7
9	14	Block 1	350	0.4	0.7	4
24	15	Block 1	439	0.6	0.4	7
44	16	Block 1	439	0.6	0.4	8.5
47	17	Block 1	261	0.6	1.0	8.5

49	18	Block 1	350	0.4	0.7	8.5
61	19	Block 1	261	0.2	0.4	10
50	20	Block 1	350	0.4	0.7	8.5
29	21	Block 1	350	0.4	0.7	7
66	22	Block 1	439	0.2	1.0	10
46	23	Block 1	439	0.2	1.0	8.5
67	24	Block 1	261	0.6	1.0	10
45	25	Block 2	261	0.2	1.0	8.5
48	26	Block 2	439	0.6	1.0	8.5
12	27	Block 2	350	0.4	0.7	4
32	28	Block 2	350	0.4	0.7	7
2	29	Block 2	439	0.2	0.4	4
25	30	Block 2	261	0.2	1.0	7
68	31	Block 2	439	0.6	1.0	10
62	32	Block 2	439	0.2	0.4	10
52	33	Block 2	350	0.4	0.7	8.5
22	34	Block 2	439	0.2	0.4	7
5	35	Block 2	261	0.2	1.0	4
42	36	Block 2	439	0.2	0.4	8.5
51	37	Block 2	350	0.4	0.7	8.5
31	38	Block 2	350	0.4	0.7	7
72	39	Block 2	350	0.4	0.7	10
11	40	Block 2	350	0.4	0.7	4
65	41	Block 2	261	0.2	1.0	10
43	42	Block 2	261	0.6	0.4	8.5
23	43	Block 2	261	0.6	0.4	7
28	44	Block 2	439	0.6	1.0	7
63	45	Block 2	261	0.6	0.4	10
71	46	Block 2	350	0.4	0.7	10
3	47	Block 2	261	0.6	0.4	4
8	48	Block 2	439	0.6	1.0	4
17	49	Block 3	350	0.4	0.3	4
33	50	Block 3	200	0.4	0.7	7
20	51	Block 3	350	0.4	0.7	4
14	52	Block 3	500	0.4	0.7	4
56	53	Block 3	350	0.8	0.7	8.5
74	54	Block 3	500	0.4	0.7	10
40	55	Block 3	350	0.4	0.7	7
16	56	Block 3	350	0.8	0.7	4
77	57	Block 3	350	0.4	0.3	10
75	58	Block 3	350	0.0	0.7	10
54	59	Block 3	500	0.4	0.7	8.5
80	60	Block 3	350	0.4	0.7	10
60	61	Block 3	350	0.4	0.7	8.5
38	62	Block 3	350	0.4	1.2	7
34	63	Block 3	500	0.4	0.7	7
13	64	Block 3	200	0.4	0.7	4
53	65	Block 3	200	0.4	0.7	8.5

19	66	Block 3	350	0.4	0.7	4
57	67	Block 3	350	0.4	0.3	8.5
59	68	Block 3	350	0.4	0.7	8.5
78	69	Block 3	350	0.4	1.2	10
79	70	Block 3	350	0.4	0.7	10
76	71	Block 3	350	0.8	0.7	10
73	72	Block 3	200	0.4	0.7	10
35	73	Block 3	350	0.0	0.7	7
55	74	Block 3	350	0.0	0.7	8.5
58	75	Block 3	350	0.4	1.2	8.5
37	76	Block 3	350	0.4	0.3	7
15	77	Block 3	350	0.0	0.7	4
18	78	Block 3	350	0.4	1.2	4
39	79	Block 3	350	0.4	0.7	7
36	80	Block 3	350	0.8	0.7	7

3.4 Data Analysis

RSM was applied to evaluate the effects of flow rate, ozone dose, and influent concentrations of iron and manganese on the removal efficiencies of iron and manganese removal by the PWDU. The Design-Expert software program version 8.0 (Stat-Ease) was used to analyze the data generated based on the experimental design (see Tables 3.3 and 3.4).

A CCD uses the method of least squares regression to fit the data to a quadratic model. The quadratic model for the response (removal efficiency, R) was as follows:

$$Y = a_0 + \sum_{i=1}^{3} a_i X_i + \sum_{i=1}^{3} a_{ii} X_{ii} + \sum_{i=1}^{3} a_{ij} X_{ij} \quad (3.3)$$

where Y represents the response variable, a_0 is a constant, ai, aii and aij are the linear, quadratic and interactive coefficients, respectively; X_i and X_j are the levels of the independent variables. The software uses this quadratic model to build the response surface. The adequacy of the model was determined by evaluating the lack of fit, coefficient of determination (P-value) and the Fisher test value (F-value) obtained from

the analysis of variance (ANOVA) that was generated by the software. Statistical significance of the model and model parameters was determined at the 5% probability level ($\alpha = 0.05$). Three-dimensional surface response plots were generated by varying two variables within the experimental range while holding the other constant at the central point. Experimental data was analyzed by multiple regressions to fit the quadratic equation to all independent variables. Analysis of variance (ANOVA) was performed to evaluate significant differences between independent variables. To visualize the relationship between the responses and the independent variables, surface response and contour plots of the fitted quadratic regression equations were generated using Design-Expert software version 8.0.

In detail, the following steps were carried out to conduct the analysis following the recommendation of the Design-Expert software manual (Stat-Ease, Minneapolis, MN) (Design-Expert Software, 2012):

i. The transformation is only carried out when required. In this study, no data transformation was carried out for the analysis of iron removal efficiency, while power transformation was carried out for the analysis of manganese removal efficiency.

ii. The model was selected based on the results of sequential F-tests, lack-of-fit tests and other adequacy measures.

iii. ANOVA, along with post-ANOVA analysis of individual model coefficients and case statistics were performed for analysis of residuals and outlier detection.

iv. Diagnostic plots including normal probability plot of residuals, residuals vs. predicted, residuals vs. run, and predicted vs. actual were inspected to statistically validate the model.

v. If a model is validated, the model graphs are generated, i.e., the contour and 3D graphs, for interpretation. The models were inspected to see if they are appropriate for the data distribution. An appropriate model must be significant and the lack-of-fit must be insignificant. The various coefficient of determination, R^2 values should be close to 1. The diagnostic plots should also exhibit trends associated with a good model and these will be elaborated subsequently.

Following the analysing of each response, multiple response optimization was performed, either by inspection of the interpretation plots, or with the graphical and numerical tools provided for this purpose.

The test for significance of the regression model is performed as an ANOVA procedure by calculating the F-ratio, which is the ratio between the regression mean square and the mean square error. The F-ratio, also called the variance ratio, is the ratio of variance due to the effect of a factor (in this case the model) and variance due to the error term. This ratio is used to measure the significance of the model under investigation with respect to the variance of all the terms included in the error term at the desired significance level α. A significant model is required for further analysis.

The test for significance on individual model coefficients forms the basis for model optimisation by adding or deleting coefficients through backward elimination, forward addition or stepwise elimination/ addtion/ exchange. It involves the determination of the P-value or probability value, usually relating the risk of falsely rejecting a given

hypothesis. For example, a "Prob. > F" value on an F-test tells the proportion of time you would expect to get the stated F-value if no factor effects are significant. The "Prob. > F" value determined can be compared with the desired probability or α-level. In general, the lowest order polynomial would be chosen to adequately describe the system.

In order to test for the lack-of-fit, replicate measurements were analyzed to determine the significance of replicate error in comparison to the model-dependent error. This test splits the residual or error sum of squares into two portions, one which is due to pure error which is based on the replicate measurements and the other due to lack-of-fit based on the model performance. The test statistic for lack-of-fit is the ratio between the lack-of-fit mean square and the pure error mean square. Similarly, this F-test statistic can be used to determine as to whether the lack-of-fit error is significant or otherwise at the desired significance level α. Insignificant lack-of-fit is desired as significant lack-of-fit indicates that there might be contributions in the regressor–response relationship that are not accounted for by the model.

In addition, checks need to be made in order to determine whether the model actually describes the experimental data (Steppan et al., 1998). The checks performed here include determining the various coefficient of determination, R^2. These R^2 coefficients have values between 0 and 1. In addition to the above, the adequacy of the model is also investigated by the examination of residuals (Montgomery, 1997). The residuals, which are the difference between the respective, observe responses and the predicted responses are examined using the normal probability plots of the residuals and the plots of the residuals versus the predicted response. If the model is adequate, the points on the normal probability plots of the residuals should form a straight line. On the

other hand, the plots of the residuals versus the predicted response should be structureless, suggesting the absence of any they should contain no obvious patterns.

CHAPTER 4 RESULTS AND DISCUSSION

Aiming to improve the treatment of raw water for rural communities by the PWDU system, this study evaluated the removal efficiencies of iron and manganese by this system as a function of flow rate, ozone dose, and influent iron and manganese concentrations. To evaluate the effects of these parameters, a total of 80 testing runs were carried out using a central composite design approach. During these testing runs, the influent water with the determined concentrations of iron and manganese were treated by the PWDU under varying flow rate and ozone dose, and the effluent concentrations of iron and manganese were monitored by ICP-MS. The removal efficiencies for iron and manganese in each run were calculated and serve as the response variables. The results from the PWDU trials performed as per the experimental plan are shown in Table 4.1. Although both removal efficiency and net removal rate were calculated for iron and manganese, only removal efficiency was selected for further analysis as net removal rate is not an idenpendent variable from influent concentration or flow rate. These results were analyzed using the Design Expert software 8.0®, and the test for significane of the regression model, test for significane on invidivual model coefficients, and test for lack of fit were carried out following the procedures outlined in section 3.4. The results for iron and manganese removal efficiencies are summarized in Tables 4.2 and 4.3, respectively. The results of the analyses suggest that while the removal efficiencies for iron were affected by both the iron and manganese concentrations in the raw water, the effects of flow rate or ozone dosage on iron removal efficiency were not significant (Table 4.2). On the other hand, the manganese removal efficiency was significantly ($p < 0.05$) affected by

all 4 factors as well as the interaction between influent manganese concentration and flow rate (Table 4.3). In addition, the analyses also showed that the iron and manganese concentrations in the influent and flow rate negatively affected the manganese removal efficiency, with the impact being the greatest for influent iron concentration, followed by influent manganese concentration, and flow rate. In terms of the effect of ozone dose on manganese removal, higher ozone dosages seemed to improve manganese removal efficiencies except when the ozone dosage reached maximum (i.e. 10g/hr).

Table 4.1 Experimental Result

Run No.	Block No.	Flow rate (L/hr)	Influent conc. of Mn (mg/L)	Influent conc. of Fe (mg/L)	Ozone dose (gO3/Hr)	Net removal rate of Fe (mg/hr)	Percent Fe removed (%)*	Net removal rate of Mn (mg/hr)	Percent Mn removed (%)*
1	Block 1	350.00	0.62	1.93	10.00	178.95	42.52	65.76	40.47
2	Block 1	260.81	0.39	1.65	4.00	336.49	57.55	97.56	56.80
3	Block 1	439.19	0.39	2.22	7.00	288.95	58.43	73.73	72.28
4	Block 1	439.19	0.85	1.65	4.00	240.39	41.12	126.52	33.70
5	Block 1	260.81	0.85	2.22	4.00	339.94	68.74	128.68	57.71
6	Block 1	439.19	0.39	2.22	4.00	383.22	46.02	106.64	62.08
7	Block 1	260.81	0.39	1.65	8.50	227.13	65.42	71.87	70.46
8	Block 1	350.00	0.62	1.93	10.00	499.82	70.53	144.89	52.95
9	Block 1	439.19	0.85	1.65	10.00	292.52	62.78	123.51	41.28
10	Block 1	350.00	0.62	1.93	4.00	272.23	48.20	28.65	13.14
11	Block 1	350.00	0.62	1.93	7.00	282.56	50.03	44.77	20.53
12	Block 1	260.81	0.85	2.22	7.00	196.61	29.63	123.34	41.22
13	Block 1	260.81	0.39	1.65	7.00	124.02	46.58	33.06	42.27
14	Block 1	350.00	0.62	1.93	4.00	436.15	54.06	40.13	12.88
15	Block 1	439.19	0.85	1.65	7.00	248.46	53.33	144.77	48.38
16	Block 1	439.19	0.85	1.65	8.50	279.74	60.04	142.94	47.77
17	Block 1	260.81	0.85	2.22	8.50	404.54	60.96	149.85	50.08
18	Block 1	350.00	0.62	1.93	8.50	240.40	42.57	56.58	25.95
19	Block 1	260.81	0.39	1.65	10.00	298.69	64.11	70.98	51.85
20	Block 1	350.00	0.62	1.93	8.50	267.38	47.34	85.04	39.00
21	Block 1	350.00	0.62	1.93	7.00	243.42	57.84	57.81	35.58
22	Block 1	439.19	0.39	2.22	10.00	512.11	61.50	135.87	79.10
23	Block 1	439.19	0.39	2.22	8.50	274.14	55.44	78.66	77.12
24	Block 1	260.81	0.85	2.22	10.00	327.69	39.35	182.52	48.61
25	Block 2	260.81	0.39	2.22	8.50	244.85	49.51	63.55	62.30
26	Block 2	439.19	0.85	2.22	8.50	456.88	54.87	197.52	52.61
27	Block 2	350.00	0.62	1.93	4.00	-16.79	NA	-10.01	NA
28	Block 2	350.00	0.62	1.93	7.00	359.41	50.72	88.13	32.21
29	Block 2	439.19	0.39	1.65	4.00	299.85	64.36	76.70	56.03
30	Block 2	260.81	0.39	2.22	7.00	371.08	55.92	95.15	69.51
31	Block 2	439.19	0.85	2.22	10.00	319.02	48.07	127.95	42.76

32	Block 2	439.19	0.39	1.65	10.00	303.20	65.08	100.89	73.71
33	Block 2	350.00	0.62	1.93	8.50	172.98	53.60	47.95	38.49
34	Block 2	439.19	0.39	1.65	7.00	494.11	74.24	161.63	82.65
35	Block 2	260.81	0.39	2.22	4.00	299.59	45.14	70.81	51.73
36	Block 2	439.19	0.39	1.65	8.50	342.78	73.57	98.65	72.06
37	Block 2	350.00	0.62	1.93	8.50	313.08	55.44	81.00	37.15
38	Block 2	350.00	0.62	1.93	7.00	347.24	61.48	80.85	37.08
39	Block 2	350.00	0.62	1.93	10.00	343.10	60.75	77.81	35.68
40	Block 2	350.00	0.62	1.93	4.00	321.10	56.85	49.19	22.56
41	Block 2	260.81	0.39	2.22	10.00	148.13	29.96	66.83	65.52
42	Block 2	260.81	0.85	1.65	8.50	373.77	63.93	176.46	47.00
43	Block 2	260.81	0.85	1.65	7.00	225.39	64.92	92.57	41.52
44	Block 2	439.19	0.85	2.22	7.00	457.11	54.89	192.98	51.40
45	Block 2	260.81	0.85	1.65	10.00	160.28	46.16	90.47	40.58
46	Block 2	350.00	0.62	1.93	10.00	380.85	53.74	88.30	32.27
47	Block 2	260.81	0.85	1.65	4.00	151.22	43.56	35.62	15.97
48	Block 2	439.19	0.85	2.22	4.00	269.12	32.32	136.16	36.26
49	Block 3	350.00	0.62	1.45	4.00	208.83	52.40	73.00	33.48
50	Block 3	200.00	0.62	1.93	7.00	347.46	61.52	82.95	38.04
51	Block 3	350.00	0.62	1.93	4.00	255.71	45.28	33.07	15.17
52	Block 3	500.00	0.62	1.93	4.00	290.96	51.52	18.11	8.31
53	Block 3	350.00	1.01	1.93	8.50	202.35	62.70	90.29	44.57
54	Block 3	500.00	0.62	1.93	10.00	317.32	39.33	163.71	52.56
55	Block 3	350.00	0.62	1.93	7.00	272.97	48.33	117.18	53.74
56	Block 3	350.00	1.01	1.93	4.00	304.81	53.97	139.03	39.21
57	Block 3	350.00	0.62	1.45	10.00	214.37	53.79	47.44	21.75
58	Block 3	350.00	0.24	1.93	10.00	353.46	62.59	56.04	68.71
59	Block 3	500.00	0.62	1.93	8.50	174.67	30.93	-33.59	NA
60	Block 3	350.00	0.62	1.93	10.00	358.71	63.51	121.30	55.63
61	Block 3	350.00	0.62	1.93	8.50	208.93	49.64	54.49	33.53
62	Block 3	350.00	0.62	2.41	7.00	366.78	39.98	130.95	47.86
63	Block 3	500.00	0.62	1.93	7.00	253.96	60.35	88.89	54.71
64	Block 3	200.00	0.62	1.93	4.00	228.45	32.24	65.57	23.96
65	Block 3	200.00	0.62	1.93	8.50	206.50	49.07	57.36	35.30
66	Block 3	350.00	0.62	1.93	4.00	347.06	48.97	48.71	17.80
67	Block 3	350.00	0.62	1.45	8.50	178.07	59.96	74.66	45.95
68	Block 3	350.00	0.62	1.93	8.50	301.84	42.59	2.05	0.75
69	Block 3	350.00	0.62	2.41	10.00	408.87	55.93	143.19	65.67
70	Block 3	350.00	0.62	1.93	10.00	196.99	34.88	-5.54	NA
71	Block 3	350.00	1.01	1.93	10.00	156.17	27.65	46.12	13.01
72	Block 3	200.00	0.62	1.93	10.00	292.94	51.87	50.33	23.08
73	Block 3	350.00	0.24	1.93	7.00	202.32	62.69	35.70	76.60
74	Block 3	350.00	0.24	1.93	8.50	467.75	57.98	106.91	91.77
75	Block 3	350.00	0.62	2.41	8.50	274.60	37.56	134.46	61.66
76	Block 3	350.00	0.62	1.45	7.00	238.96	59.96	101.71	46.65
77	Block 3	350.00	0.24	1.93	4.00	327.17	57.93	55.15	67.62
78	Block 3	350.00	0.62	2.41	4.00	231.25	31.63	60.00	27.52
79	Block 3	350.00	0.62	1.93	7.00	287.30	50.87	62.06	28.46
80	Block 3	350.00	1.01	1.93	7.00	337.54	59.77	125.36	35.36

*In 4 cases, negative removal efficiency values were resulted due to fluctuations in background conconcentrations of iron and maganese. The removal efficiency values for these cases were denoted as "NA" and were removed from further analysis.

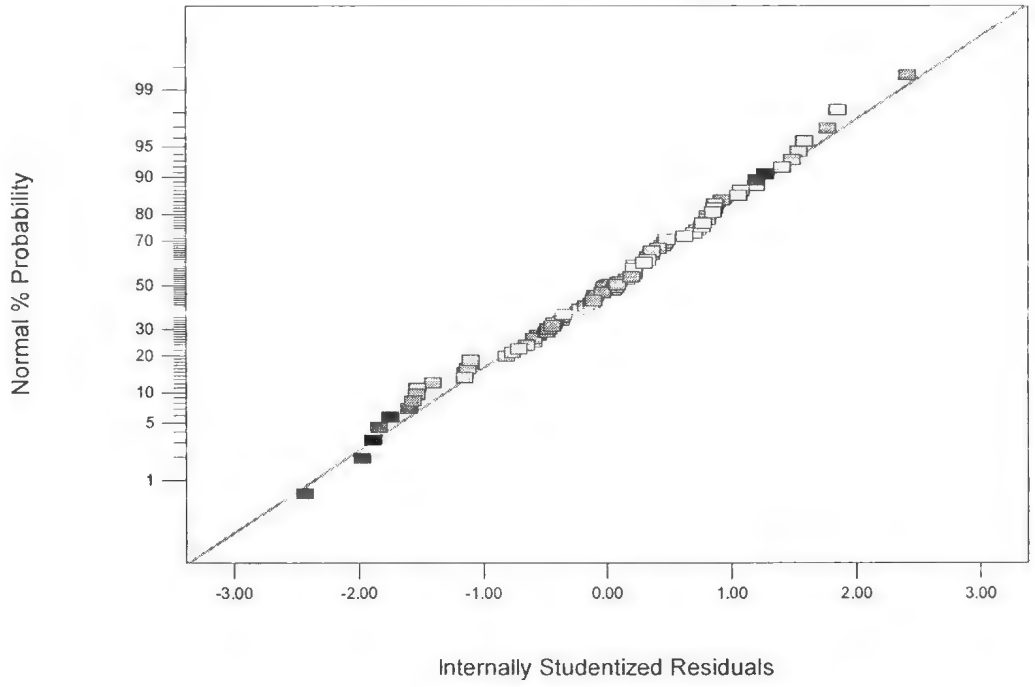
4.1 Statiscal Analysis of Iron Removal Efficiency and Model Fitting

In order to determine the suitability of the proposed model (See section 3.3.4 for details) in recapitulating the interations between experimental conditions (i.e. flow rate, ozone dose, influent concentrations of iron and managanese) and results (i.e. effluent concentrations of iron and managanese) in drinking water treatment to remove iron and manganese, statistical analyses were carried out to determine the fitness of the model. Any siginificant model terms were selected to fit the model, while insignificant terms were eliminated (i.e. model reduction) from the model. During evaluation of the effects of various terms on iron removal efficiency, the concentrations of Mn (i.e. term B) and Fe (i.e. term C) had significant effects on the removal efficiency, whereas other insignificant terms were excluded from the model and assigned as residual (Table 4.2). The inspection of the model showed that the fitted model was both significant and adequate (see detailed explanation below).

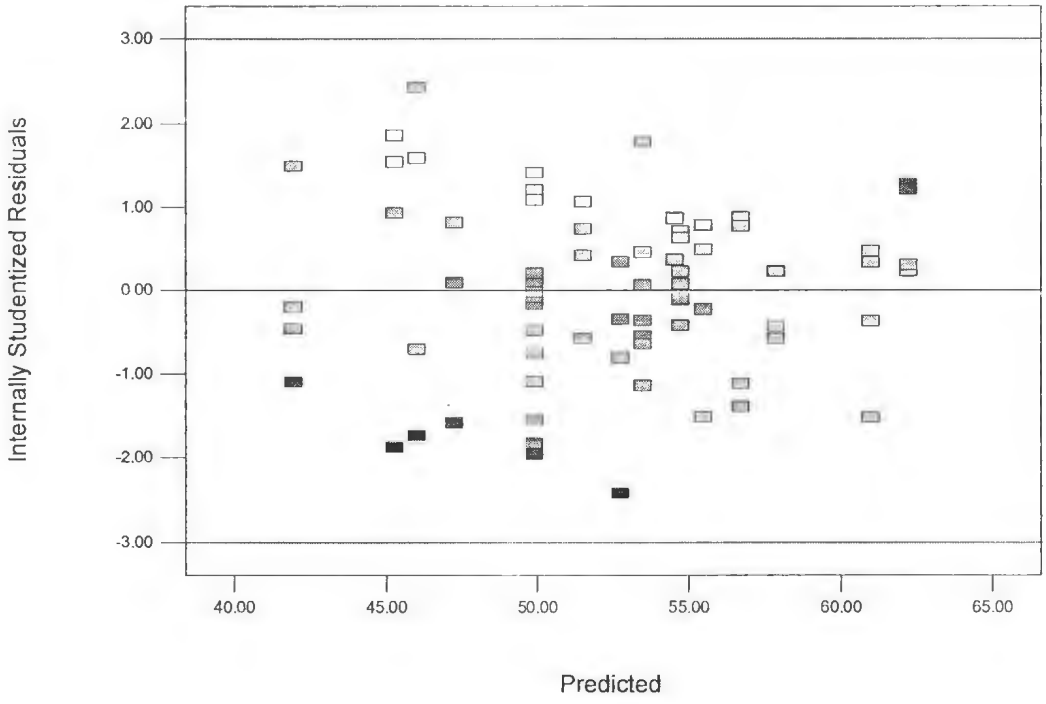
Table 4.2 Results of ANOVA test for response surface reduced linear model of iron removal efficiency

Source	Sum of Square	Df	Mean Squares	F Value	p-value Prob > F	
Block	352.39	2	176.19			
Model	1639.00	2	819.50	8.54	0.0005	Significant
B-Conc. Mn	414.81	1	414.81	4.32	0.0411	
C-Conc. Fe	1224.19	1	1224.19	12.76	0.0006	
Residual	7100.10	74	95.95			
Lack of Fit	6119.75	63	97.14	1.09	0.4706	Not significant
Pure Error	980.34	11	89.12			
Cor Total	9091.48	78				
Std. Dev.	9.80	R-Squared		0.1875		
Mean	52.41	Adj R-Squared		0.1656		
C.V. %	18.69	Pred R-Squared		0.0676		
PRESS	8147.96	Adeq Precision		8.227		

The Model F-value of 8.54 (Table 4-2) suggested that this model was significant as this value translates to a 0.05% probability that the Model F-Value was generated by noise. Difference between Adj R^2 and Pred R^2 less than 0.2 indicates this model was adequate. Values of "Prob > F" that were less than 0.05 indicate model terms are significant. Prob > F values less than 0.05 for cases B and C (Table 4-2) suggested that they were significant model terms. Therefore, the influent concentrations of iron and manganese were important factors in terms of the removal efficiency in the response surface reduced linear model. On the other hand, model terms flow rate and ozone dose had "Prob > F" values that were greater than 0.1, which indicated these model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may be conducted to improve this model. The "Lack of Fit F-value" of 1.09 was also obtained, impling the insignificance relative to the pure error.


Normal % Probability
99
95
90
80
70
50
30
20
10
5
1
-3.00
-2.00
-1.00
0.00
1.00
2.00
3.00
Internally Studentized Residuals

(a)


Internally Studentized Residuals
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1.00
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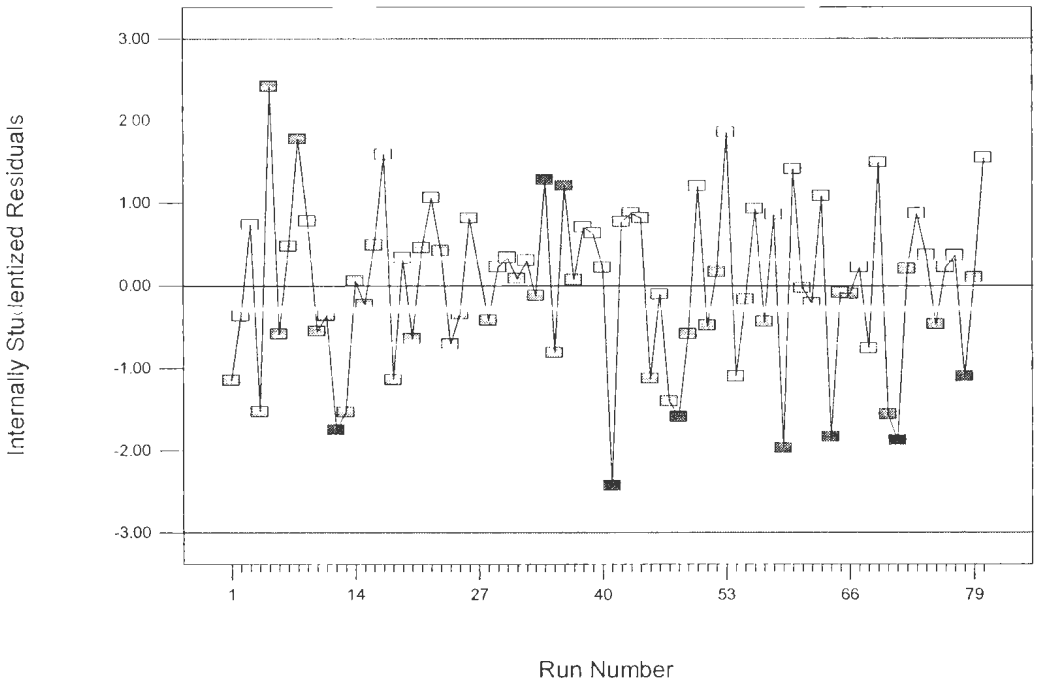
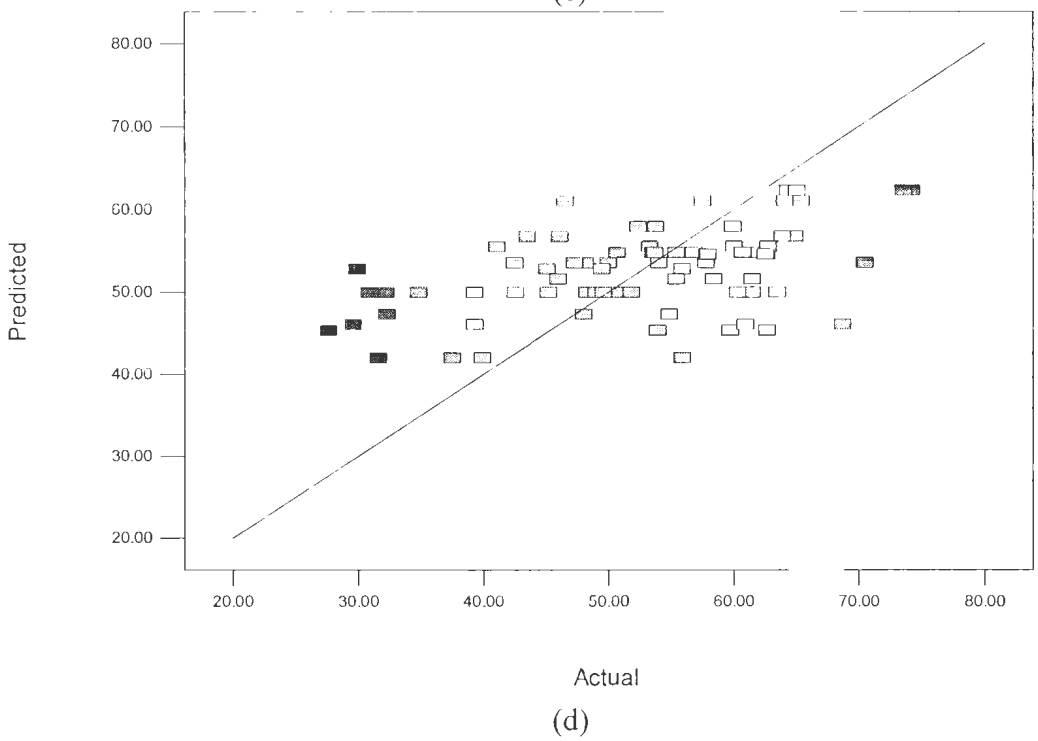
-1.00
-2.00
-3.00
40.00
45.00
50.00
55.00
60.00
65.00
Predicted

(b)



(c)



(d)

Figure 4.1 Diagnostic plots for assumption of ANOVA: (a) normal probability plot of residuals, (b) residuals vs. predicted, (c) residuals vs. run number, and (d) predicted vs. actual

There are four main diagnostic plots to check the assumptions of ANOVA, and they are "normal probability plot of residuals", "residuals vs. predicted", "residuals vs. run", and "predicted vs. actual" (Figure 4.1). Viewed from Figure 4.1(a), all the residuals are distributed close to a straight line; therefore, the normal distribution assumption is satisfied. In Figure 4.1b, because all the residual points are scattered randomly all over the graph within the upper and lower bounds instead of accumulating in the other areas, the assumption of homoscedasticity is fulfilled. Figure 4.1c shows that all the residual points are spread within upper and lower bounds without any patterns, indicating that the independence assumption is satisfied. In Figure 4.1d, all the points are close to the straight line within the measurement, showing that the model fits well. Therefore, all the diagnostic plots indicate that all the required assumptions of ANOVA are met.

The regression equation obtained from the ANOVA of the CCD response model based on the results from 80 trials was obtained as follows:

Final equation in terms of coded factors:

$R_1 = +52.72 - 2.76 * B - 4.73 * C$ (4.1)

which can be converted to a final equation in terms of actual factors:

$R_1 = +84.41914 - 11.98095 *$ Conc. Mn $- 16.61014 *$ Conc. Fe (4.2)

The coefficients for each of the significant factor (i.e. influent concentrations of Mn and Fe) can provide valuable information on the contribution of these factors to the response. In this case, the negative coefficient for the influent concentrations of both manganese and iron suggested that these factors had negative impacts on the iron removal efficiency. In addition, the magnitude of the coefficient for influent iron concentration (-

16.61014) is greater than of influent manganese concentration (-11.98), which indicated that the effect of influent iron concentration on iron removal efficiency was greater than of influent manganese concentration. In order to explain these results, the source of soluble iron as well as the mechanism of iron removal by the PWDU needs to be discussed. Although iron commonly exists in the form of ferric iron in nature, reduced form of iron, known as siderite ($FeCO_3$), is also present.

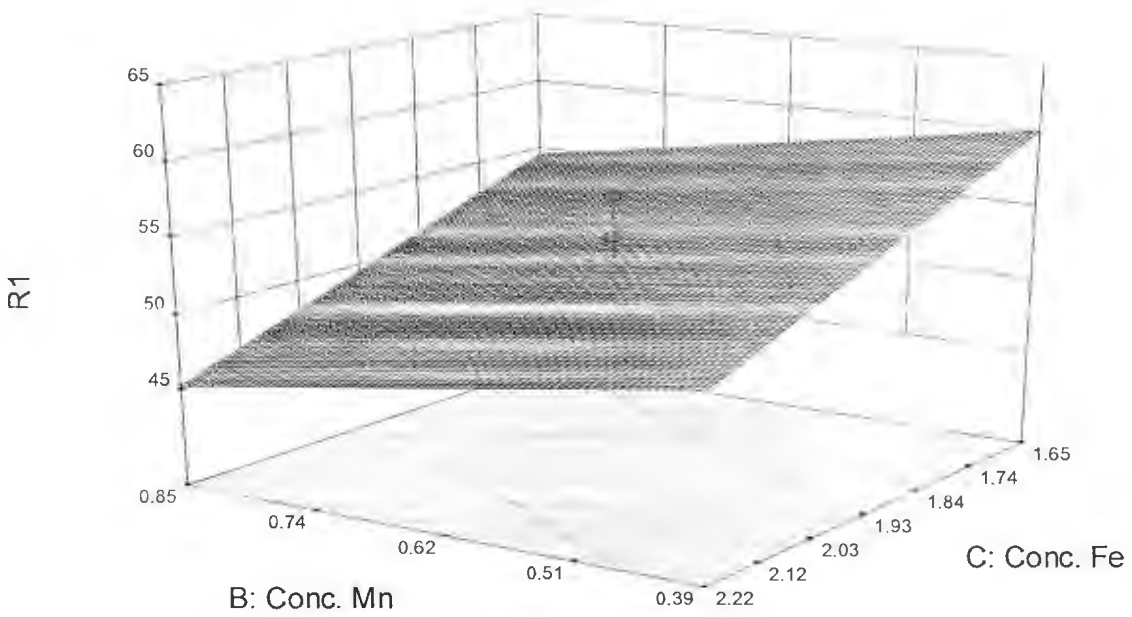
$$FeCO_3 + CO_2 + H_2O \rightarrow Fe(HCO_3)_2 \quad (4.3)$$

In water, the siderite can react with carbon dioxide to form ferrous bicarbonate (Equation 4.3), especially in anaerobic conditions. In order to remove ferrous bicarbonate from water, the PWDU in this study uses ozone (O_3) as the oxidizing agent to convert soluble ferrous bicarbonate to insoluble ferric iron that ultimately forms insoluble ferric hydroxide in water (Equation 4.4). Similar results were also reported previously (AWWA, 1990). Based on this equation, it was estimated that 0.43 mg of ozone is consumed in order to oxidize 1 mg of ferrous iron. Among all the testing runs conducted in this study, the lowest ozone dose used was 4 g/hr, which is theoretically sufficient to convert as much as 9,032 mg of iron per hour. This capacity exceeded the highest possible amount of ferrous iron entered the PWDU at 1,205 mg per hour (calculated by multiplying the maximum flow rate by highest ferrous iron concentration) by more than 7 fold. Since it is known that in a neutral environment, the oxidization of ferrous iron is thermodynamically favourable given sufficient amount of ozone, it is not surprising that the differences in ozone dose among testing runs had little effect on the iron removal efficiency as the lowest ozone dose was already sufficient to oxidize the highest possible amount of

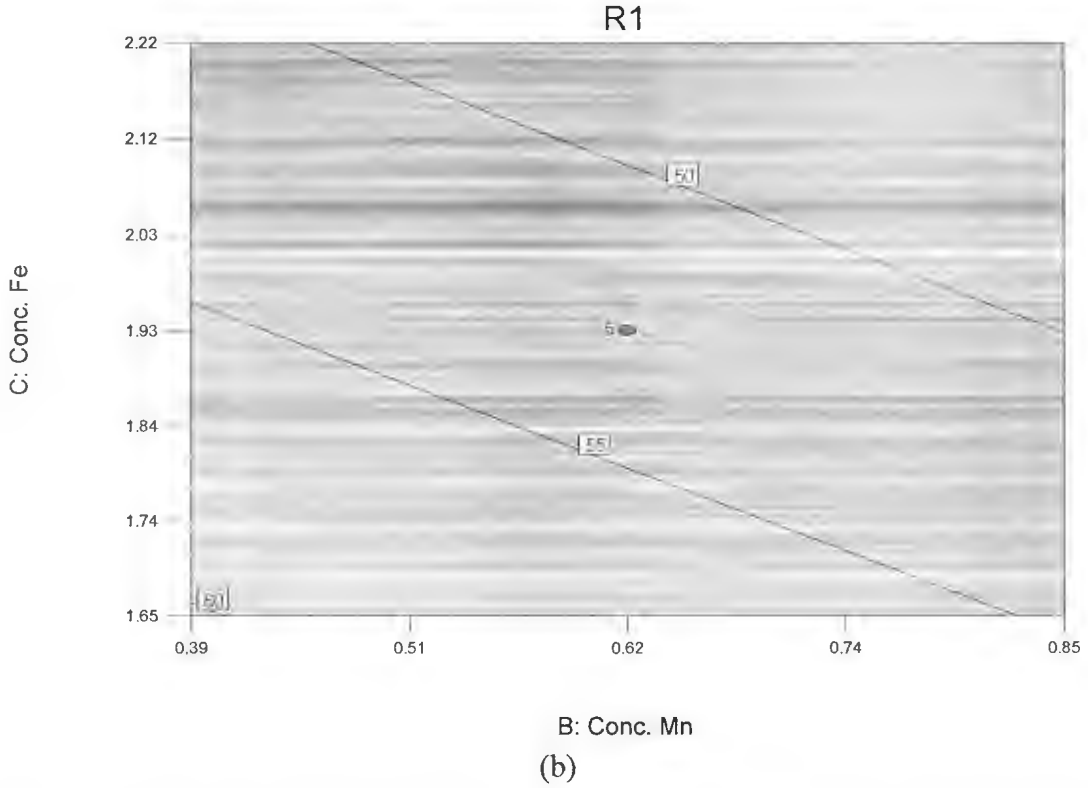
ferrous iron used. In agreement with this explanation, the flow rate did not have any effect on iron removal efficiency suggesting sufficient contact for oxidizing the ferrous iron, and sufficient time for ferric iron to be precipitated and removed from the system. Since neither the amount of oxidizing reagent nor the reaction time appeared to be limiting factors, the negative effects of influent iron and manganese concentrations on iron removal efficiency may be caused by other limiting factors. It is possible that subsequent treatment procedures may be sensitive to higher concentrations of iron and/or manganese. For example, the multimedia filter or activated carbon filter in the subsequent treatment procedures could be saturated at higher iron/manganese dosages. However, as the iron concentration was only assessed for the effluent, not at any intermediate stages, whether a specific treatment stage had restricted the removal efficiency would require a more comprehensive study that focuses on each of the treatment stages in the future. Since the influent was largely composed of tap water, which may contain other organic or inorganic impurities that may affect iron removal efficiency in a concentration-dependent manner.

$$2Fe^{2+} \xrightarrow{O_2 \rightarrow O_2} 2Fe^{3+} \xrightarrow{H_2O} Fe(OH)_3 \downarrow \quad (4.4)$$

Graphical representations of the regression equation, the response surfaces and the contour plot were also obtained using Design-Expert software version 8.0, which are presented as Figure 4.2. Consistent with the regression equation, the graphical representations also showed the negative relationships between iron removal efficiency and influent iron and manganese concentrations.



(a)



(b)

Figure 4.2 The iron removal efficiency by PWDU as functions of influent iron and manganese concentrations presented as: (a) a three dimensional surface model plot and (b) a contour plot.

4.2 Statiscal Analysis of Manganese Romoval Efficiency and Model Fitting

Similar to the analyses that were carried out to model iron removal efficiency of PWDU, the effects of potential parameters on manganese removal efficiency were also evaluated. Based on the initial analysis using a Box-Cox plot approach, power transformation was recommended by the analytical software (i.e. Design Expert) to improve the fitness of the model. Specifically, the recommeded power law transformation based on the Box-Cox plot was $y'=y^{\lambda}$, and the exponent lambda in the equation was obtained at the minimum point of the curve generated by the natural log of the sum of squares of the residuals. If the 95% confidence interval around this lambda included 1, no specific transformation would be recommended. In this particular study, the Box-Cox plot (Figure 4.3) required power transformation as $\lambda=1$ was not located in the 95% confidence interval. Therefore, according to the Box-Cox plot (Figure 4.3) the model needs to be power transformed, and the value of λ that minimized the error sum of squares is 1.46, resulting a recommended power law transformation $y'=y^{1.46}$.

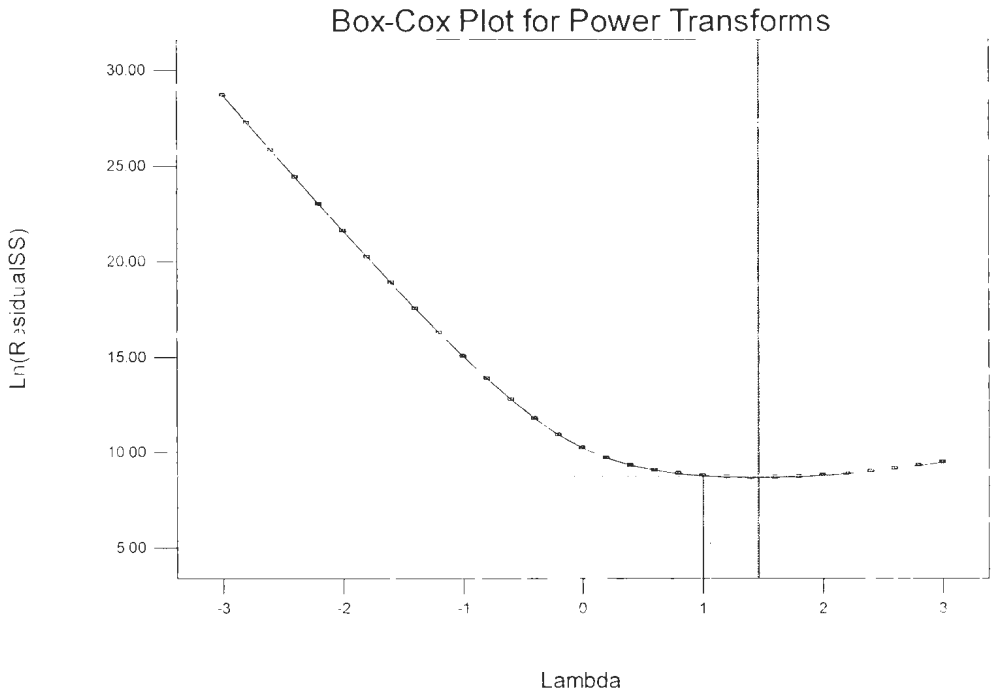


Figure 4.3 The Box-Cox plot for iron removal efficiency

It was previously mentioned that the test for significance of the regression model, the test for significance on individual model coefficients, and the test for lack of fit need to be preformed. Similar to the analysis conducted to determine the respone in terms of iron removal efficiency, the backwards elimiation procedure was selected to automatically reduce the terms that are not significant (not counting those required to support hierarchy), and the resulting ANOVA table for the reduced quadratic model for manganese removal efficiency is shown in Table 4.3.

Table 4.3 Results of ANOVA for response surface reduced quadratic model of manganese removal efficiency

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Block	5228.04	2	2614.02			
Model	1.757E+005	10	17573.74	19.22	< 0.0001	Significant
A-Flow Rate	5210.86	1	5210.86	5.70	0.0200	

B-Conc. Mn	70111.17	1	70111.17	76.66	< 0.0001	
C-Conc. Fe	5807.88	1	5807.88	6.35	0.0142	
D-Ozone Dose	23562.52	3	7854.17	8.59	< 0.0001	
AB	2969.05	1	2969.05	3.25	0.0763	
A^2	5948.01	1	5948.01	6.50	0.0132	
B^2	54164.23	1	54164.23	59.23	< 0.0001	
C^2	19747.43	1	19747.43	21.59	< 0.0001	
Residual	58530.79	64	914.54			
Lack of Fit	50817.60	54	941.07	1.22	0.3887	not significant
Pure Error	7713.19	10	771.32			
Cor Total	2.395E+005	76				
Std. Dev.	30.24	R-Squared		0.7502		
Mean	110.24	Adj R-Squared		0.7111		
C.V. %	27.43	Pred R-Squared		0.6382		
PRESS	84759.32	Adeq Precision		15.527		

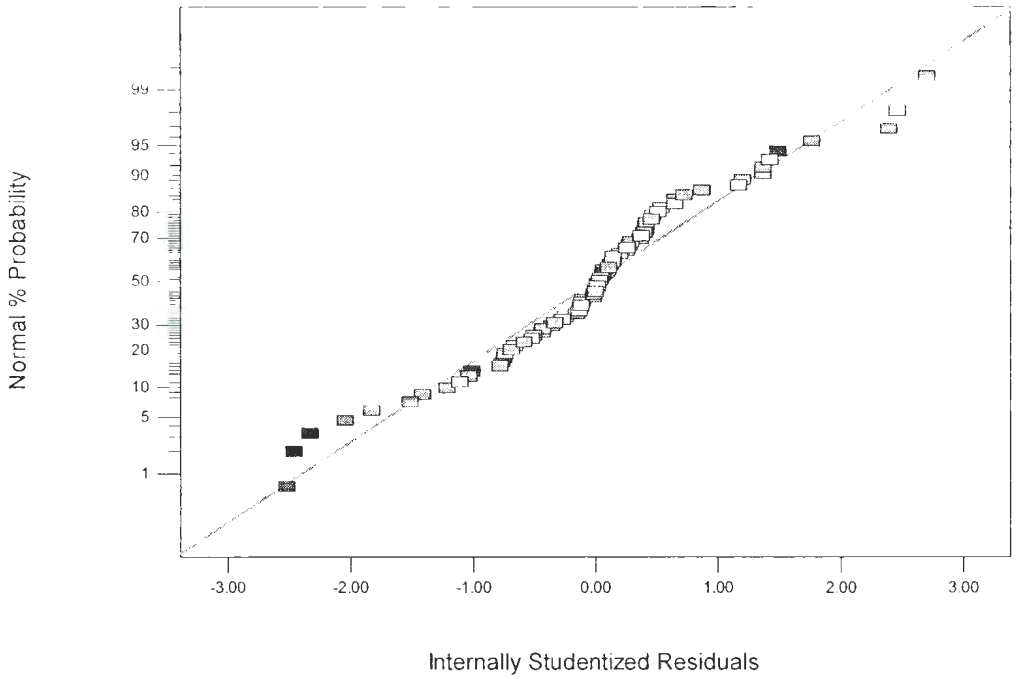
Results from Table 4.3 indicate that the model is still significant as the Model F-value of 19.22 translates to a 0.01% chance that a "Model F-Value" this large could occur due to noise.

Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A, B, C, D, A^2, B^2, C^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. The main effect of A (flow rate), B (concentration of manganese), C (concentration of iron), and D (ozone dose), the second-order effect of A^2 B^2 C^2 and the interaction of flow rate and manganese concentration (AB) are the significant model terms.

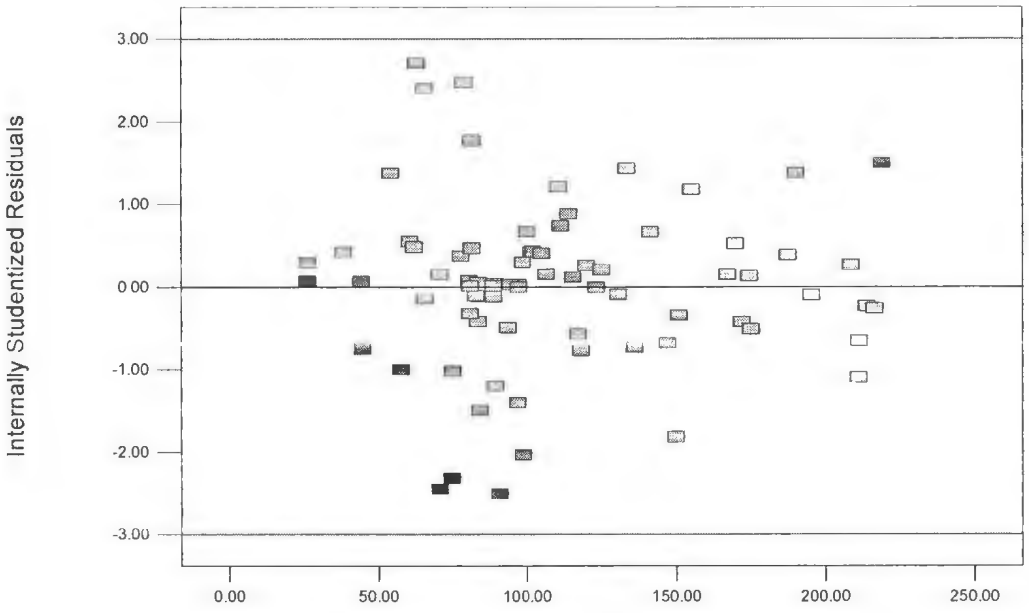
Additionally, the results show that the second order effects of flow rate (A^2) concentration of iron (B^2) concentration of manganese (C^2) and the interaction between the flow rate and manganese concentration provide secondary contribution to the manganese removal efficiency. The "Lack of Fit F-value" of 1.22 implies the lack of fit is not significant relative to the pure error, (Table 4.3). This non-significant lack of fit

agrees with the fitness expectation of the model. An R^2 value of 1 is ideal as it translates to a perfect linearity. In this analysis, the R^2 is 0.7502 (Table 4.3), suggesting high degrees of linearity. In addition, the predicted R^2 is in reasonable agreement with the adjusted R^2. The adjusted R^2 value is particularly useful when comparing models with different number of terms. This comparison is however done in the background when model reduction is taking place. Adequate precision compares the range of the predicted values at the design points to the average prediction error. Ratios greater than 4 indicate adequate model discrimination, and this was true for the model.

There are four main diagnostic plots to check the assumptions of ANOVA, and they are "normal probability plot of residuals", "residuals vs. predicted", "residuals vs. run", and "predicted vs. actual" (Figure 4.4)



(a)


Internally Studentized Residuals
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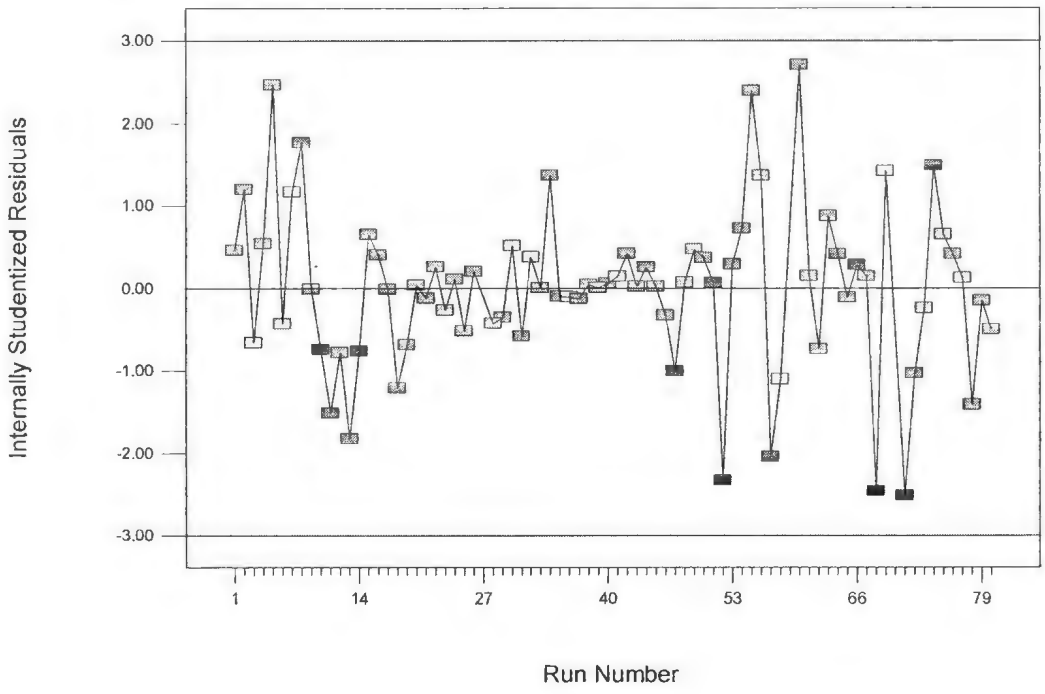
2.00
1.00
0.00
-1.00
-2.00
-3.00
0.00
50.00
100.00
150.00
200.00
250.00
Predicted

(b)


Internally Studentized Residuals
3.00
2.00
1.00
0.00
-1.00
-2.00
-3.00
1
14
27
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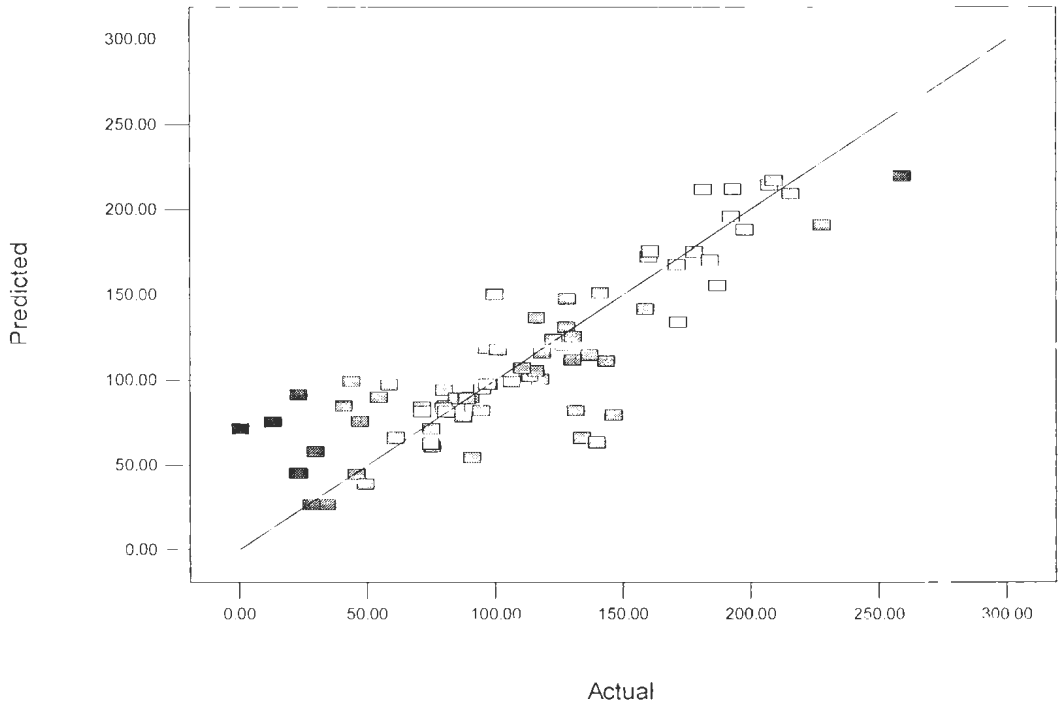
66
79
Run Number

(c)



(d)

Figure 4.4 Diagnostic plots for assumption of ANOVA: (a) normal probability plot of residuals, (b) residuals vs. predicted, (c) residuals vs. run, and (d) predicted vs. actual

Viewed from Figure 4.4a, all the residuals are close to the straight line; therefore, the normal distribution assumption is satisfied. In Figure 4.4b, because all the residual points are scattered randomly all over the graph within the upper and lower bounds instead of accumulating in the other areas, the assumption of homoscedasticity is fulfilled. Figure 4.4c indicates that all the residual points are spread within upper and lower bounds, showing no patterns. This plot approves that the independence assumption is satisfied. In Figure 4.4d, all the points are close to the straight line, showing that the "predicted vs. actual" plot is satisfactory and the model fits well. This implies that the models proposed are adequate and there is no reason to suspect any violation of the independence or constant variance assumption. Therefore, all the required assumptions of ANOVA are met.

Comparing the mean square against an estimate of the experimental error tested the statistical significance of factors and their interactions. Therefore, the effects having p-values less than 0.1, indicating that these were significantly different from zero at the 90% confidence level, were excluded from the model and assigned as residual. The lack-of-fit test was used to determine whether the constructed models were adequate to describe the observed data. The test is performed by comparing the variability of the current model residuals to the variability between observations at replicate settings of the factors. When the estimated p-value for the lack-of-fit is less than 0.05, there is statistically significant lack-of-fit at the 95% confidence level. That means that the model does not adequately represent the data. The R-squared statistic indicates the percentage of the variability of the optimization parameter that is explained by the model.

While, the following equations are the final empiraical models in terms of coded factors for iron removal efficiency R_2,

$(R_2)^{1.46} = +156.24+32.74 * A-106.44 * B+29.54 * C-83.38 * D[1]+23.77 * D[2]+42.10 * D[3]-30.56 * AB+29.94 * A^2+89.90 * B^2+51.40 * C^2$ (4.5)

Final Equation in Terms of Actual Factors:

Ozone Dose 4 gO_3/Hr

$(R_2)^{1.46} = +2145.86-1.66 *$ Flow Rate-1312.70 * Conc. Mn-1940.40 * Conc. Fe -1.48 * Flow Rate * Conc. Mn+3.76E-003 * Flow Rate^2+1671.75 * Conc. Mn^2 +632.83 * Conc. Fe^2 (4.6)

Ozone Dose 7 gO_3/Hr

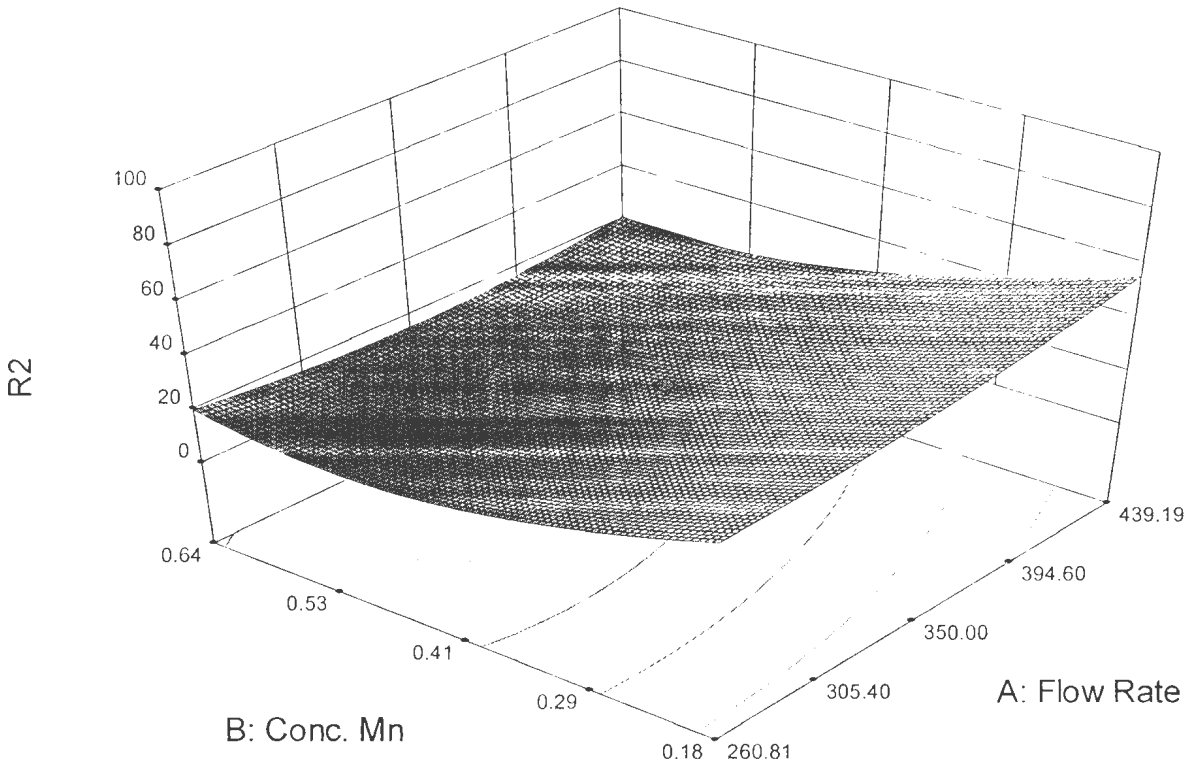
$(R_2)^{1.46} = +2253.02 -1.66 *$ Flow Rate -1312.70 * Conc. Mn-1940.40 *Conc. Fe -1.48 * Flow Rate * Conc. Mn+3.76E-003 * Flow Rate^2+1671.75 *Conc. Mn^2+632.83 * Conc. Fe^2(4.7)

Ozone Dose 8.5 gO_3/Hr

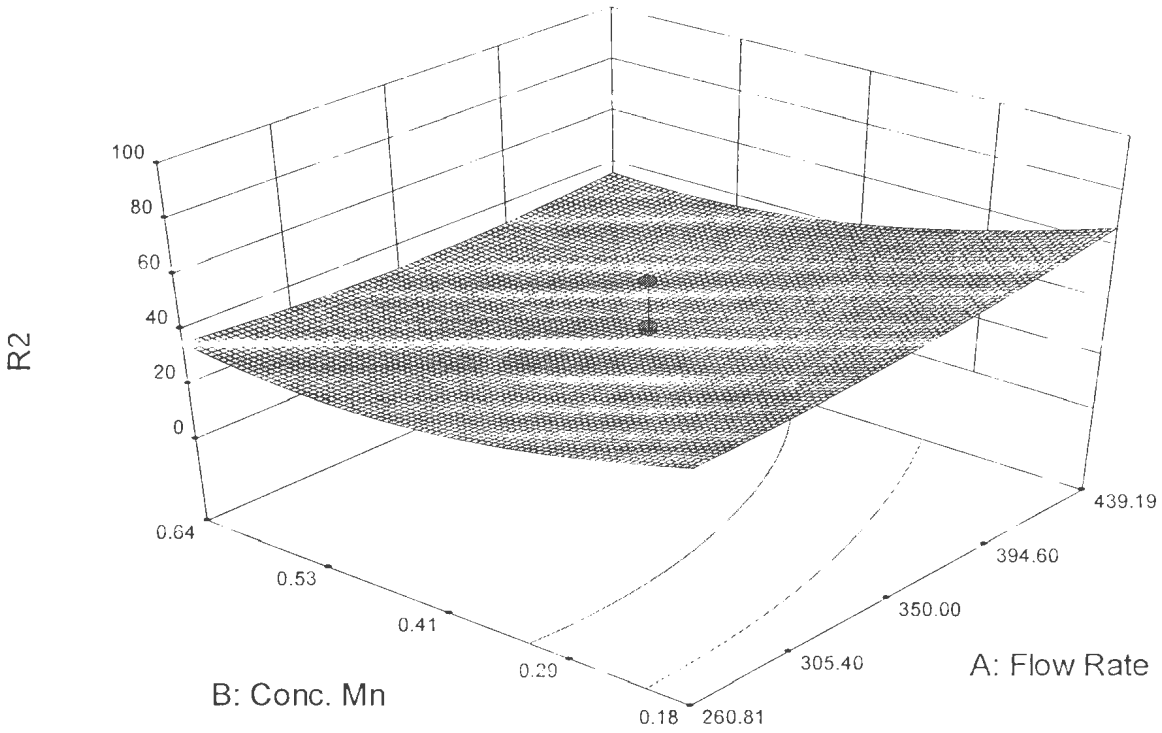
$(R_2)^{1.46} = +2271.35-1.66 * \text{Flow Rate} -1312.70 * \text{Conc. Mn}-1940.40 * \text{Conc. Fe} -1.48 * \text{Flow Rate} * \text{Conc. Mn}+3.76E-003 * \text{Flow Rate}^2+1671.75 * \text{Conc. Mn}^2+632.83 * \text{Conc. Fe}^2$ (4.8)

Ozone Dose 10 gO_3/Hr

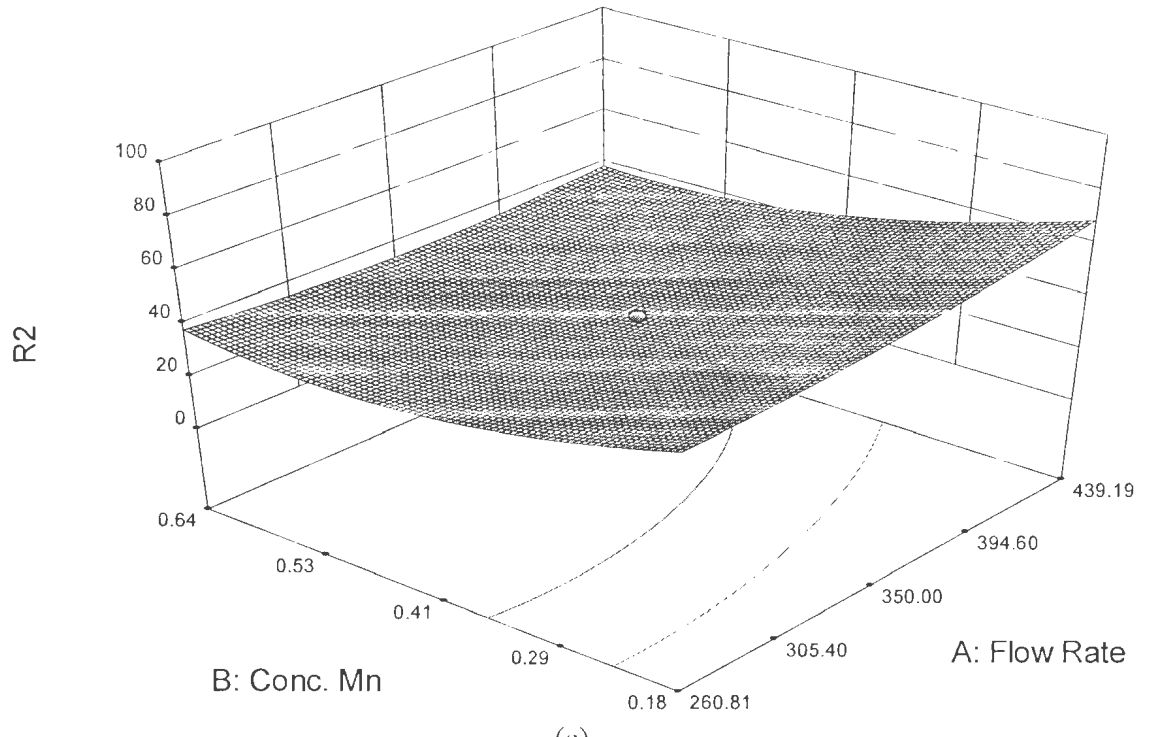
$(R_2)^{1.46} = +2246.75-1.66 * \text{Flow Rate}-1312.70* \text{Conc. Mn}-1940.40 * \text{Conc. Fe} -1.48 * \text{Flow Rate} * \text{Conc. Mn}+3.76E-003 * \text{Flow Rate}-+1671.75*\text{Conc. Mn}^2+632.83*\text{Conc. Fe}^2$ (4.9)



(a)


R2
100
80
60
40
20
0
0.64
0.53
0.41
0.29
0.18
B: Conc. Mn
260.81
305.40
350.00
394.60
439.19
A: Flow Rate

(b)


R2
100
80
60
40
20
0
0.64
0.53
0.41
0.29
0.18
B: Conc. Mn
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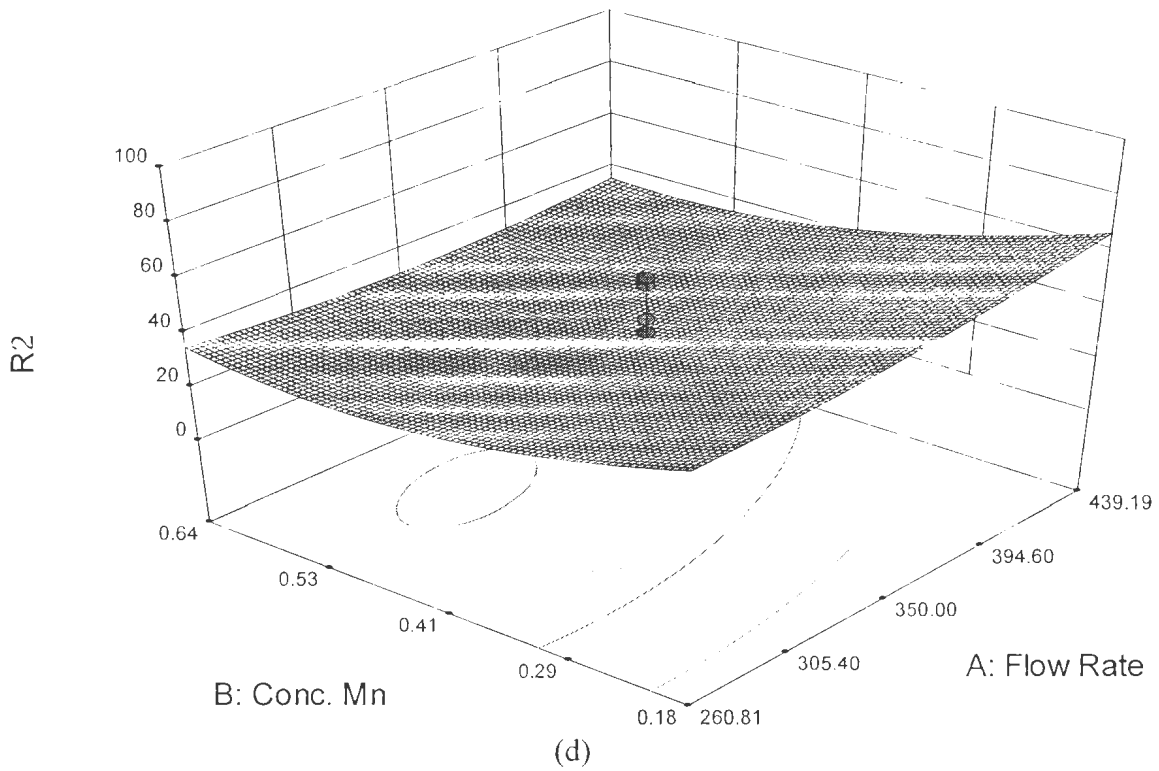
350.00
394.60
439.19
A: Flow Rate

(c)

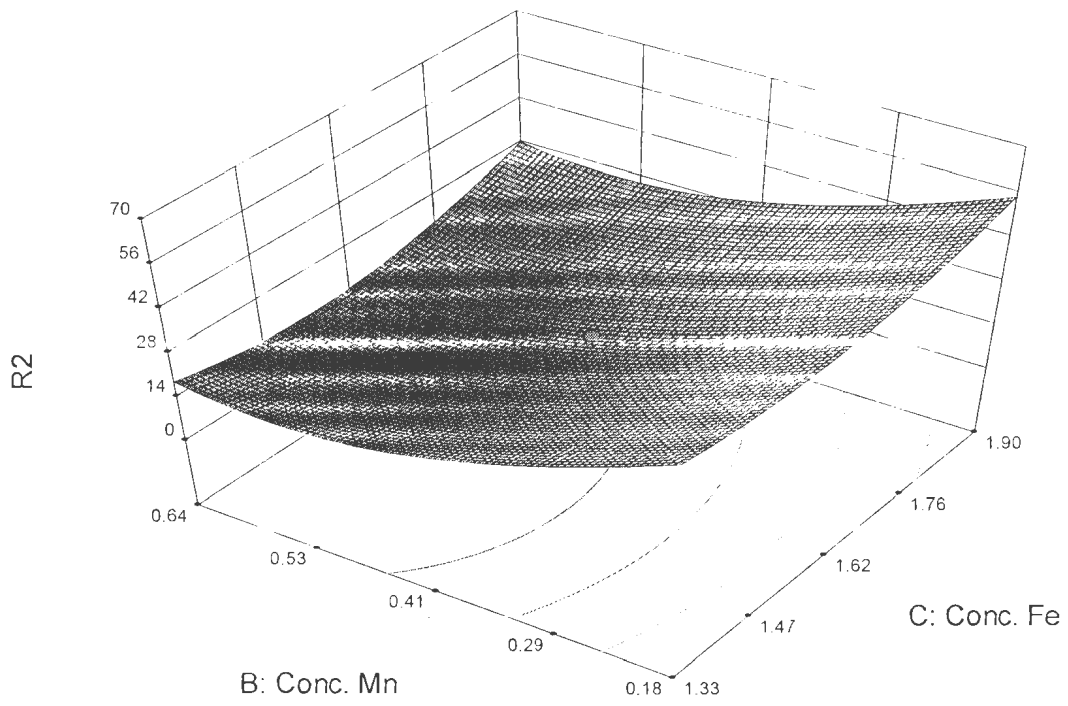


(d)

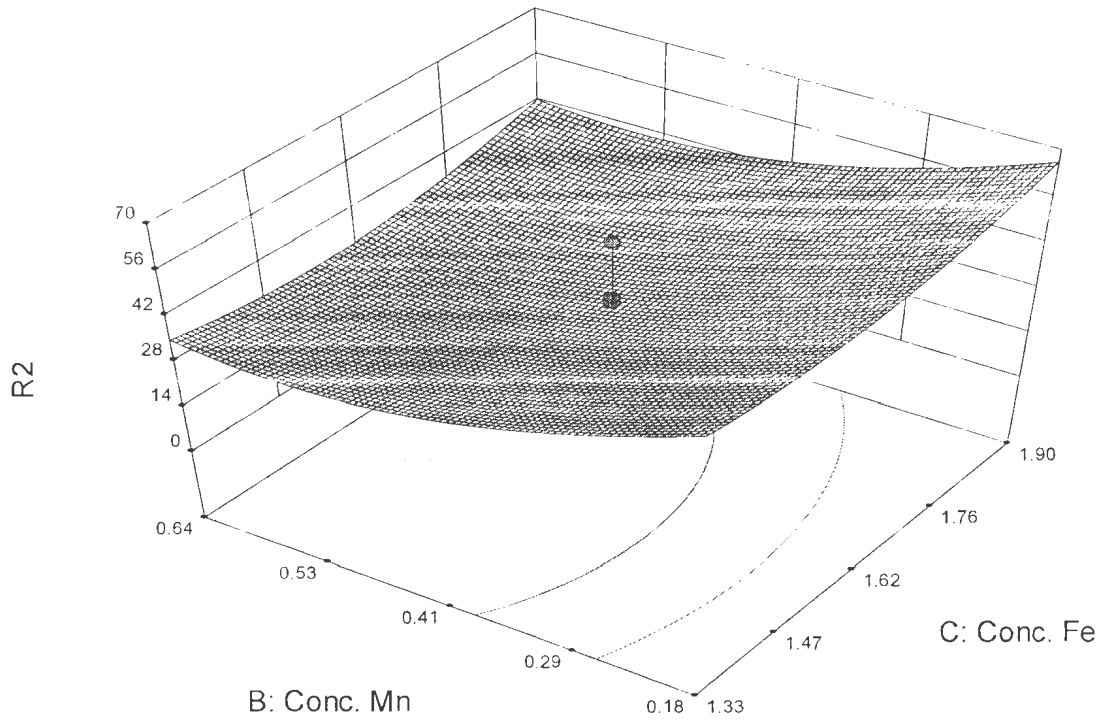
Figure 4.5 The manganese removal efficiency by PWDU as functions of flow rate and influent manganese concentration represented by surface model plots at 4 different ozone dosages: (a) 4g/hr, (b) 7g/hr, (c) 8.5g/hr, and (d) 10g/hr.

Similar to the equations that were generated based on the analyses conducted for iron removal efficiency; coefficients for significant factors were also generated for the manganese removal efficiency model. However, this model is much more complicated in comparison to the iron removal efficiency model as all 4 parameters were shown to have significant effects on the response variable (i.e. manganese efficiency). In addition, second order effects of flow rate (A^2), concentration of iron (B^2), and concentration of manganese (C^2) and the interaction between the flow rate and manganese concentration (i.e. AB) also had significant effects on manganese removal efficiency. Since the ozone dose is a categorical instead of a numeric variable, 4 equations in terms of actual factors were generated for 4 different ozone dosages based on a generalized equation in terms of

coded factors. These 4 equations were graphically represented using response surfaces plots (Figure 4.5 a-d). For all equations in terms of actual factors, the coefficients for flow rate, and influent concentrations of iron, and manganese are all negative (-0.53 for flow rate, -725.72 for influent manganese concentration, and -858.84 for influent iron concentration), indicating their negative effects on the manganese removal efficiency. These coefficients also indicate that the magnitude of effects was highest for influent concentration of iron followed by influent concentration of manganese, while the effect of flow rate manganese removal efficiency is relatively small. This observation is confirmed by the response surface plots for all ozone dosages, as the removal efficiency slope along the axis representing influent concentration of manganese is much steeper than its slope along the axis representing flow rate, suggesting that the influent concentration of manganese has a greater impact on the manganese removal efficiency than flow rate for all ozone doses (Figure 4.5, a-d).


R2
70
56
42
28
14
0
0.64
0.53
0.41
0.29
0.18
B: Conc. Mn
1.33
1.47
1.62
1.76
1.90
C: Conc. Fe

(a)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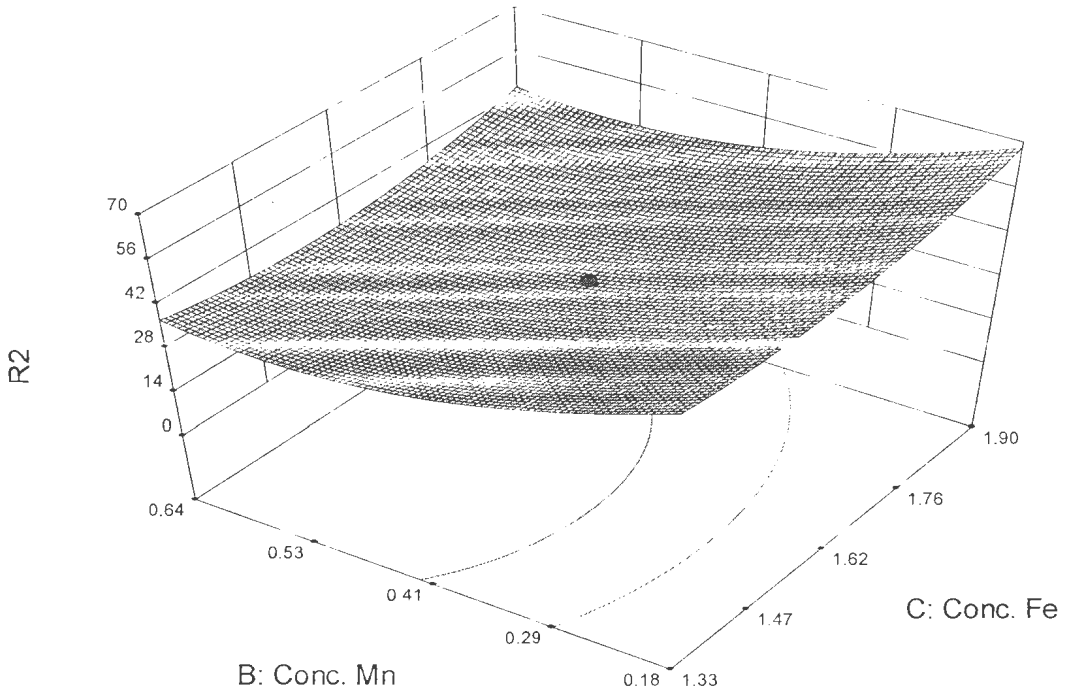
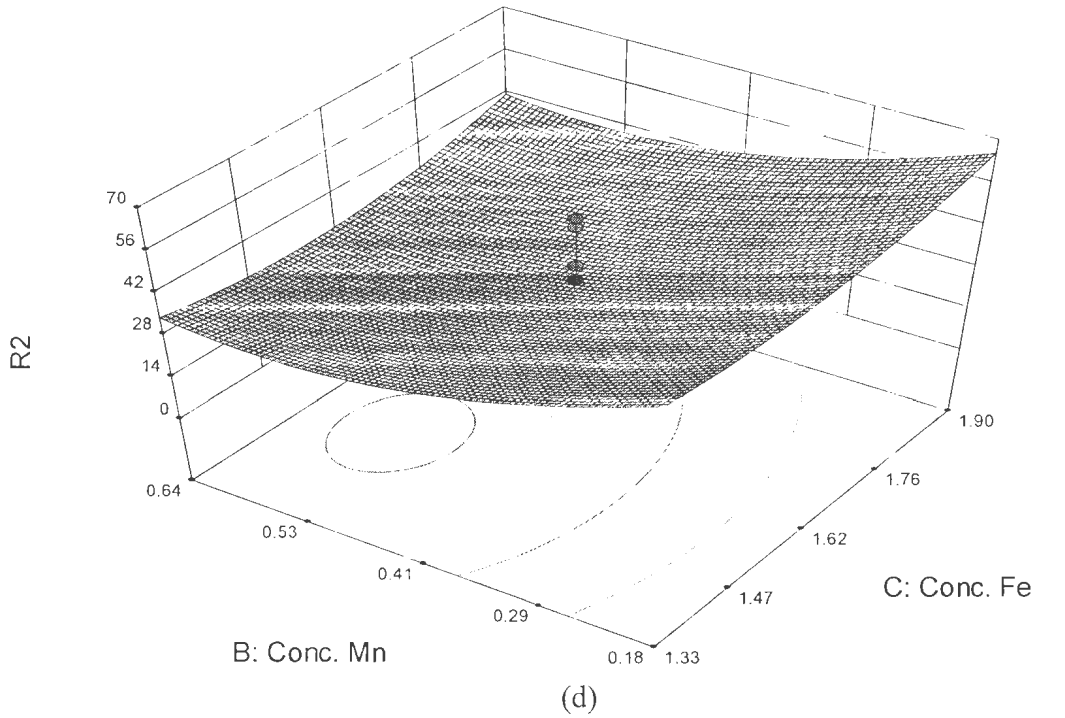
(b)



(c)



(d)

Figure 4.6 The manganese removal efficiency by PWDU as functions of influent iron and influent manganese concentration represented by surface model plots at 4 different ozone dosages: (a) 4g/hr, (b) 7g/hr, (c) 8.5g/hr, and (d) 10g/hr at center point of flow rate.

Although the effect of influent iron concentration on manganese removal efficiency may be greater than the effect of influent manganese concentration (Equation 4.4 – 4.8), the response surface plots for removal efficiency as a function of influent iron and manganese concentrations demonstrated that the effects of these factors on manganese removal efficiency is highly dependent upon ozone dosage (Figure 4.6 a-d). These response surface plots showed that, at low ozone dosage (i.e. 4 g/hr, Figure 4.6, a), the effect of influent manganese plays a more significant role in affecting manganese removal efficiency as the slope along the manganese concentration axis is much more steeper than that the iron concentration axis. This trend became much less obvious when the ozone dose increased, as the slope along the influent manganese concentration became much more gradual at higher ozone dosages (i.e. 7 g/hr or greater, Figure 4.6, b.d). In addition, these response surface plots also revealed that ozone may play a limiting role at a low dosage (e.g. 4g/hr or less) but not at higher dosages, as the manganese removal efficiency suffered significantly more (slightly above 14%, Figure 4.6, a) at low ozone dosage and high influent manganese concentration (than the cases than cases where ozone dosages were higher (slightly greater than 28%, Figure 4.6, b-d). Although the final equation showed that the increase in flow rate generally had a negative effect on manganese removal efficiency, the surface response plot showed that the flow rate actually negatively correlated with manganese removal efficiency to a certain point before such trend is reversed (Figure 4.8 a-d). At such point in terms of flow rate, the manganese removal efficiency reaches the lowest. In addition, this profile is dependent upon ozone dose and iron concentration, as the flow rate at which the manganese removal efficiency is at the lowest level changes depending on ozone dose and iron concentration. Since flow

rate plays an essential part in governing the reaction time for ozonation process, it is suspected that a set of optimum values exist for ozone dose and flow rate in treatment of manganese at certain concentrations.

Since ozone dose is a categorical, thus discrete variable, it was not included in the regression model. Therefore, its effect on manganese removal efficiency cannot be determined based on its coefficient in the model equation, and an alternative approach was used instead. A three dimensional scattered plot was generated using the data from all trial runs to see if there was a general trend in manganese removal efficiency that was associated with the change in ozone dose (Figure 4.7). Although the association between manganese removal efficiency and ozone dose was largely obscured by effects of influent iron and manganese concentrations, it was clear that the manganese removal efficiency was lower when ozone dose is at 4 g/hr regardless of influent iron and manganese concentrations.

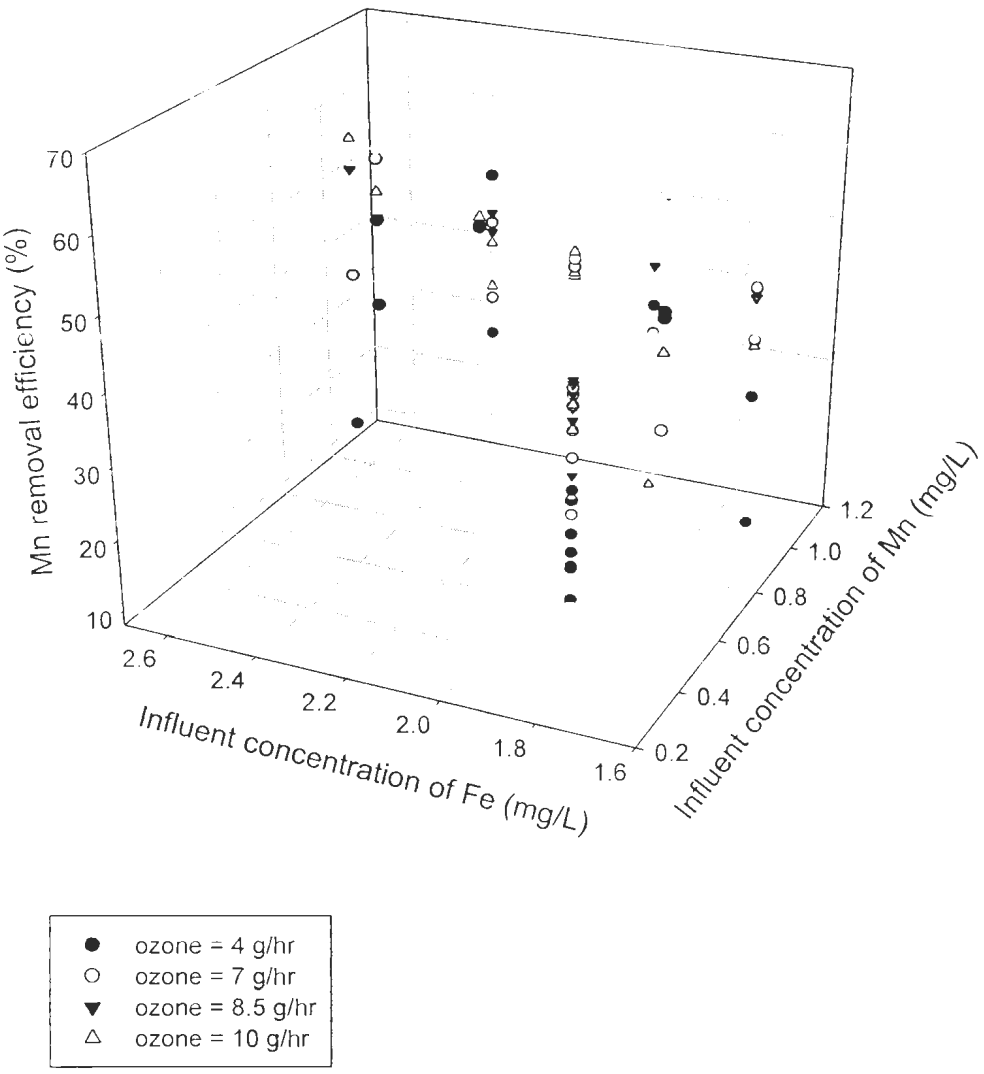


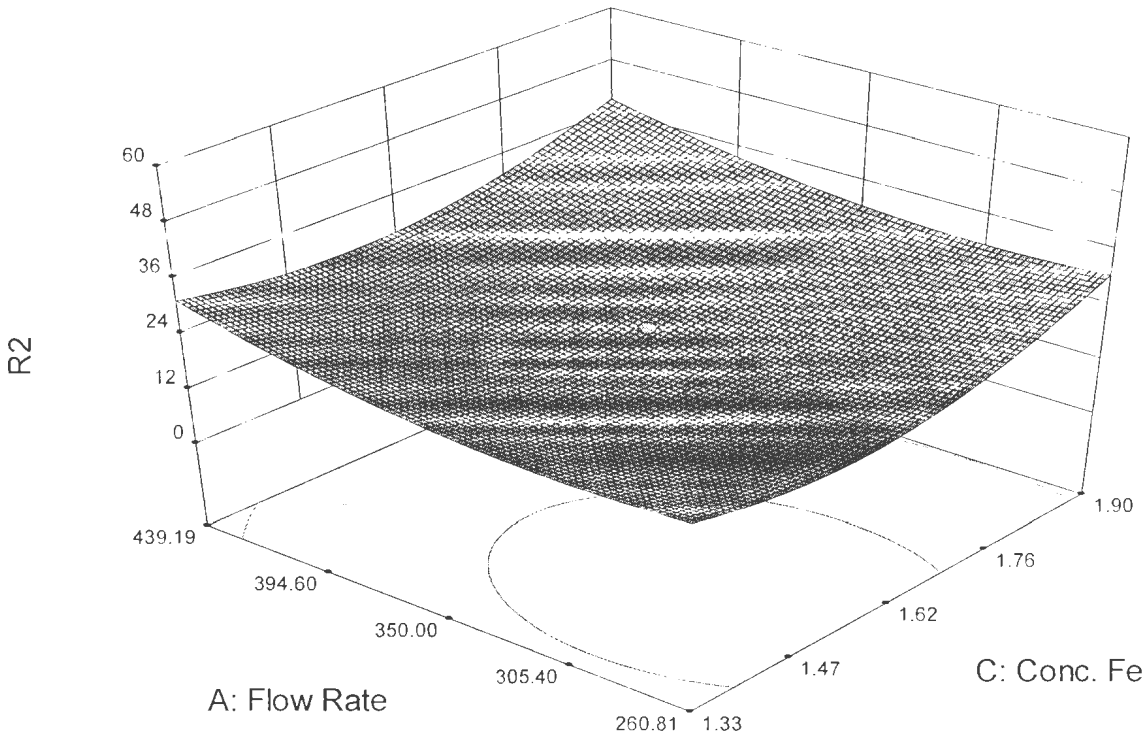
Figure 4.7 The manganese removal efficiency by PWDU at varying ozone dose, influent manganese, and iron concentrations.

$$MnCO_3 + CO_2 + H_2O \rightarrow Mn(HCO_3)_2 \quad (4.10)$$

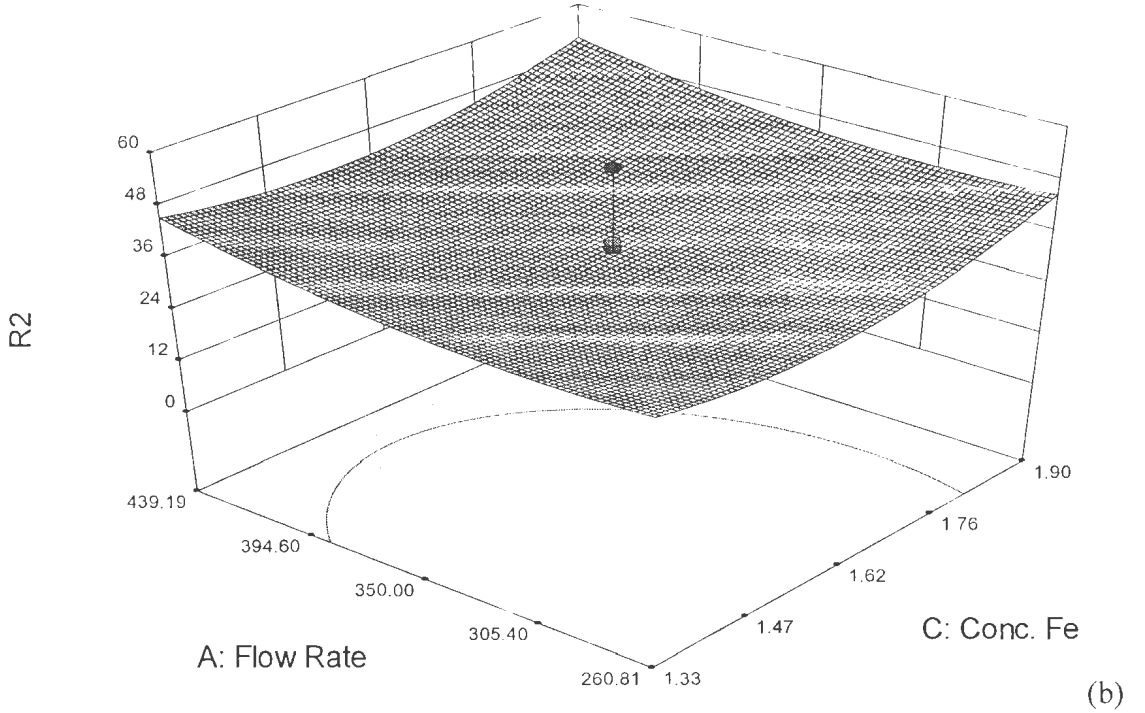
$$2Mn^{2+} \xrightarrow{O_3 + O_2} 2Mn^{4+} \xrightarrow{H_2O} MnO_2 \downarrow \quad (4.11)$$

Although oxidized manganese (Mn^{4+}) is the most prevalent form in nature, but the reduced form of manganese ($MnCO_3$), known as rhodochrosite also exists. Similar to siderite ($FeCO_3$), rhodochrosite can also react with carbon dioxide forming manganese bicarbonate that is water soluble (Equation 4.6). Also similar to the oxidation of ferrous

iron, the oxidation of manganese bicarbonate convert Mn^{2+} to Mn^{4+}, which ultimately precipitates in form of MnO_2 in water (Equation 4.7). Different from oxidization of ferrous iron, the oxidation of Mn^{2+} is much less kinetically favorable, thus it requires a longer reaction time, and it is easily outcompeted by ferrous iron (if present) for ozone. This is consistent with the negative impact of influent iron concentration on manganese removal efficiency observed in this study as increase in ferrous iron input would decrease the availability of ozone for the oxidation of manganese. In addition, more ozone (0.88 mg) is required to oxidize 1 mg of manganese than ferrous iron based on theoretical stoichiometry, which would also raise the ozone dosage requirement for sufficient oxidation of manganese. This is also consistent with the fact that low manganese removal efficiencies were observed when ozone dosage was at 4g/hr. Similarly, since the increase in flow rate reduces the contact opportunity of manganese with zone as well as reaction time, the negative effect of flow rate on manganese removal efficiency is also expected. Another unique characteristic of manganese oxidation is that manganese has the potential to be oxidized to permanganate (Mn^{7+}) if the oxidizing power is too strong. Since permanganate is highly soluble, the over-dosage of ozone or pro-longed reaction time would re-solubilize manganese. (Langlais et al., 1991). On the other hand, ferric iron is not affected by oxidation. Although the interaction between ozone dose and influent manganese concentration had no significant effect on manganese removal efficiency, it was significantly affected by the interaction between flow rate and influent manganese removal efficiency. This observation suggested that, at least for the ranges of manganese concentration and ozone dosages tested, the reaction time (i.e. affected by flow rate) had more effects on the oxidation of manganese than the ozone dose.


R2
60
48
36
24
12
0
439.19
394.60
350.00
305.40
260.81
A: Flow Rate
1.33
1.47
1.62
1.76
1.90
C: Conc. Fe

(a)


R2
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A: Flow Rate
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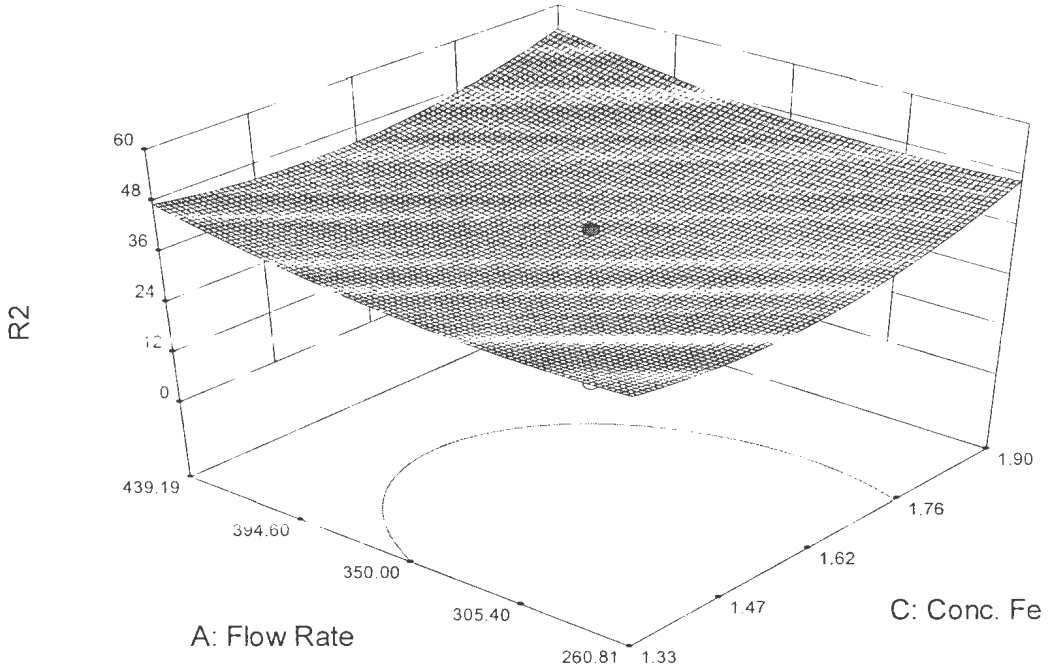
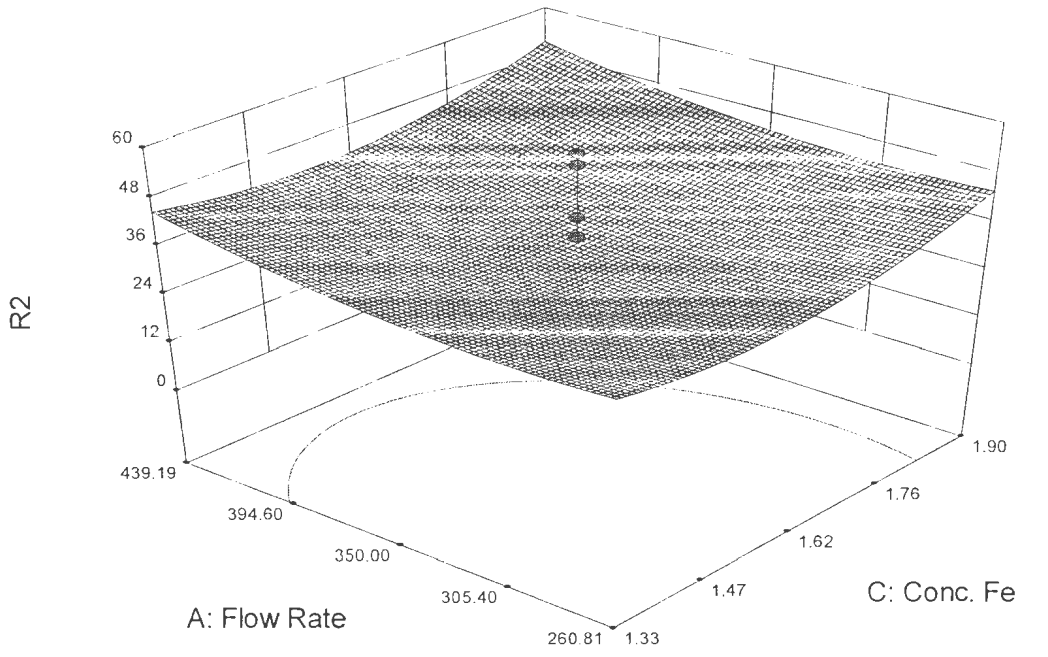
C: Conc. Fe

(b)



(c)



(d)

Figure 4.8 The manganese removal efficiency by PWDU as functions of influent iron and influent manganese concentration represented by surface model plots at 4 different ozone dosages: (a) 4g/hr, (b) 7g/hr, (c) 8.5g/hr, and (d) 10g/hr at center point of flow rate

Table 4.2 Ozone dosage and flow rate for iron and manganese removal at various influent iron and manganese concentrations

Conc. Mn (mg/L)	Conc. Fe (mg/L)	Ozone Dose	Flow Rate	Fe % removal	Mn % removal	Desirability
0.2	1.5	8.5 gO3/Hr	439.17	57.1266	66.1777	0.529
0.2	1.6	8.5 gO3/Hr	434.17	55.4663	65.7274	0.499
0.3	1.6	8.5 gO3/Hr	439.17	54.278	54.7101	0.362
0.3	1.7	7 gO3/Hr	436.9	52.617	54.0293	0.333
0.4	1.7	8.5 gO3/Hr	435.32	51.4287	47.0286	0.224
0.4	1.8	8.5 gO3/Hr	436.57	49.7677	50.3237	0.251
0.4	1.9	8.5 gO3/Hr	439.17	48.1067	55.059	0.276
0.5	1.8	8.5 gO3/Hr	436.86	48.5794	45.1079	0.165
0.5	1.9	8.5 gO3/Hr	426.49	46.9184	48.7584	0.195
0.6	1.9	8.5 gO3/Hr	433.22	45.7301	48.0962	0.17
0.6	2	8.5 gO3/Hr	439.03	44.069	54.4819	0.192
0.7	2	8.5 gO3/Hr	263.16	42.8807	57.7619	0.179
0.7	2.1	8.5 gO3/Hr	271.38	41.2197	63.9501	0.135
0.8	2.1	8.5 gO3/Hr	262.13	40.0312	72.5067	0.025

Since influent vary depending on the raw water extracted from ambient water bodies, iron and manganese concentrations in the influent cannot be considered operational parameters (i.e. not controllable) in reality. While the flow rate and ozone dose are the parameters that can be adjusted to achieve improved treatment results. In this study, we used design expert® optimization function was used to evaluate the potential in optimizing these operational parameters at various influent iron and manganese concentrations (14 combinations in total), and the response goals were set to maximize the removal efficiencies for iron and manganese. In terms of ozone dosage, it was shown that an ozone dose of 8.5 g/hr was optimal for all except one of the 14 cases evaluated (Table 4.4), as the only case where an ozone dose of 7 g/hr occurred when influent manganese and iron concentration were at 0.3 mg/L and 1.7 mg/L, respectively. These results suggested that, while lower ozone doses (4g/L and 7 g/L) were not optimal due to

insufficient ozonation, it is possible that some degree of ozone over-dose occurred at 10 g/hr, in which case manganese was re-dissolved by oxidization to permanganate, thus reducing manganese removal efficiency. These findings are interesting as the optimal ozone dose seemed somewhat constant regardless of the changes in influent manganese and iron concentrations, at least within the ranges tested.

In terms of flow rate, the optimization results showed that while higher flow rate helped to achieve better removal efficiencies at lower influent iron and manganese concentrations, lower flow rate was more optimal when iron and manganese concentrations respectively exceeded 0.6 mg/L and 2.0 mg/L, respectively. These observations suggest that, at low manganese and iron concentrations, higher flow rate helps to achieve better removal efficiencies. This is possibly because longer exposure to ozone may lead to re-dissolution of manganese at lower iron and manganese concentrations; while longer exposure to ozone is needed to sufficiently oxidize iron and manganese for efficient removal.

Although these optimization results provided valuable information to guide the operation of PWDU and improved removal of iron and manganese, the validity of these results in field applications remains to be further tested.

CHAPTER 5 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusion

Providing reliable drinking water to sparse, rural communities faces many challenges. In an effort to overcome such challenges in NL, a small scale drinking water system, the PWDU was developed and tested at various sites across NL. While the water quality produced by the PWDU satisfies drinking water standard, the occasional presence of color in treated water as a result of high iron and/or manganese concentrations need to be addressed. Although several studies have evaluated the performance of various SWTPs, their abilities in removal of iron and/or manganese had not been investigated prior to this study. In order to solve the technical challenge in iron and manganese removal as well as to improve our understanding in this subject, a performance study using the PWDU system was formulated. Using the response surface method and water quality data collected across NL, an experiment consisted of 80 treatment runs with 4 carefully chosen independent variables (i.e. flow rate, ozone dose, and influent concentrations of iron and manganese) were designed and performed. The effects of these 4 independent variables on iron and manganese removal efficiencies (calculated based on the data obtained by ICP-MS) were analyzed using a response surface methodological approach. In terms of iron removal efficiency, influent iron concentration had the strongest effect followed by influent manganese concentration, while flow rate and ozone dose had little effect on iron removal efficiency. Therefore, it appears that the greatest challenge that the PWDU is currently facing in terms of iron removal is to improve treatment efficiency at high iron concentrations. In terms of manganese removal efficiency assessment, all 4 factors

analyzed had significant effect but initial iron and manganese concentrations impacted the manganese removal efficiency more heavily than flow rate. Therefore, the greatest challenge that the PWDU is currently facing in terms of manganese removal is to improve treatment efficiency at high iron and manganese concentrations. Based on the experimental model, the optimization of operational parameters (i.e. flow rate and ozone dose) showed that an ozone dose of 8.5 g/hr was optimal for iron and manganese removal in most cases tested. While higher flow rate was preferred for raw water with lower iron and manganese concentrations, lower flow rate was better for raw water with higher iron and manganese concentrations. This study is the first step to evaluate the PWDU system in terms of iron and manganese removal, and it is also the first attempt to optimize operational parameters on a small scale water treatment plant to improve treatment results. The results generated from this study not only provided valuable information that will help to improve iron and manganese removal, but also serve as guidelines for future studies. The combined use of central composite design and response surface model approaches by this study proved to be effective thus can be applied to similar type of future studies.

5.2 Recommendations and Future Work

In this study, results from both the response surface model and the optimization study excluded ozone dose as a limiting factor for the sufficient removal of iron and manganese at high concentrations. In addition, the optimization study showed that lower flow rate was more optimal for higher removal efficiencies, suggesting one or more of filtration steps may be at their capacities. Whereas it is possible that one or more such

treatment stages may have served as limiting procedures when dealing with high iron and manganese concentrations, since we were not able to assess iron concentrations following each of the treatment stages, specific limiting factors could not be accurately identified. It is recommended in a future study, that water samples to be collected following each of the treatment stages to identify the treatment stage that is sensitive to increase in iron and manganese concentration. Samples can be analyzed, and the results can be assessed using the similar approaches proposed in this study.

The optimization study provided informative results in terms of providing guidance to improve iron and manganese removal efficiency in a controlled environment, but these results need to be improved and refined through field applications as there were several limitations associated with this study. Since most of the influent consisted of tap water, which had already been processed by the municipal drinking water treatment facility to remove various contaminants, thus the content of many other (i.e. except iron and manganese, which were added) minerals and dissolved organic matters were likely lower than those in the field. It is known that the presence of many of these contaminants (e.g. ammonia, nitrite, and halogens, etc.) would affect the stoichiometry of ozonation depending on the relative quantities. Such discrepancies in water quality between our experimental conditions and in the field may potentially translate to differences in many other treatment procedures including ozonation that ultimately affect overall treatment performance. Therefore, it is recommended in a future study, that the optimized operational parameters to be tested under site conditions. In addition, since it is expected that seasonal variations also likely affect raw water quality, it is recommended that testing to be carried on a seasonal basis.

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